# Influence of Molecular Mobility and Free Volume on the Oxidative Stability of Spray Dried Orange Oil

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Abbie Anna Hohman

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# Dedication

This Master's thesis is dedicated to my parents, Curt and Lisa, as I wouldn't be here if it weren't for your example. Together, your steadfast passion, ambition, and leadership has without a doubt made an impact on me and my career thus far. Thank you for simply being the best. Love you!

## Abstract

The objective of this research was to determine whether molecular mobility and/or free volume influences the oxidative stability of spray dried orange oil. Encapsulated orange oil was prepared by spray drying using maltodextrin, gum acacia and HiCAP® 100 as carrier materials. The physical properties of the spray dried orange oil were characterized by: viscosity, particle size, moisture content, volatile retention, and absolute density. The molecular mobility was determined by glass transition, free volume was measured positron annihilation lifetime spectroscopy (PALS) and orange oil oxidation was determined by gas chromatography.

The infeed viscosity and resultant particle size of the unloaded powders decreased as the molecular weight of the carrier material decreased. Differences between the viscosity of the unloaded and loaded emulsions was due to the addition of orange oil as it is less viscous than water and does not hydrate carrier materials yet contributes to the total percent spray drier infeed solids. The reconstituted emulsion particle size was much smaller than the infeed emulsion particle size due to the high shear of the atomizer in the spray drier. The moisture content and absolute density were independent of carrier material type. The moisture content increased with increasing water activity however, the absolute density was unaffected by a change in water activity. The volatile retention of the spray dried powders improved greatly upon the addition of emulsifier to the carrier wall material. The size of the molecular voids and orange oil oxidation decreased while molecular mobility increased with decreasing molecular weight of the carrier material. As the relative humidity increased, the average size of the molecular voids and the molecular mobility increased. The effect of water activity on the oxidation of spray dried carrier systems appeared to

increase to a certain point and then decrease with increasing water activity. Spray dried carrier systems that were formulated as a blend of carbohydrate and emulsifier provided a balance between molecular mobility and molecular free volume that provided the greatest protection against the oxidation of spray dried orange oil.

# Table of Contents


Acknowledgements …… i
Dedication …… ii
Abstract …… iii
Table of Contents …… v
List of Tables …… vii
List of Figures …… ix

Chapter 1: Literature Review…… 1
- Introduction …… 1
- Encapsulation …… 1
- Carrier Materials …… 2
  - Choice of Carrier Material…… 3
- Factors Affecting the Stability of Encapsulated Materials…… 3
- Phase Transitions …… 4
  - Temperature…… 4
  - Water Content…… 5
- Moisture Sorption Isotherms…… 6
  - BET Model …… 6
  - GAB Model …… 6
- Physical State Characterization of Amorphous Materials…… 7
- Determination of Glass Transition Temperature…… 8
- Molecular Mobility…… 9
- Glass transition Theories…… 10
  - Free Volume Theory…… 10
  - Kinetic Theory…… 11
- Influence of Carrier Molecular Weight on $T_g$…… 12
  - Packing Enhancers…… 12
  - Plasticization and Antiplasticization …… 13
- Positron Annihilation Lifetime Spectroscopy…… 13
- Diffusion …… 14
- Flavor Oxidation…… 15

Chapter 2: Objective & Hypotheses …… 16
Chapter 3: Materials & Methods…… 17
- Chemicals …… 17
- Preparation of Orange Oil Emulsion …… 17
- Spray Dryer Infeed Emulsion Viscosity …… 19
- Spray Dryer Infeed Emulsion Particle Size …… 19
- Spray Drying …… 19
- Storage of Spray Dried Powders…… 20
- Particle Size of Spray Dried Material …… 20
- Reconstituted Powder Emulsion Particle Size …… 20
- Volatile Retention by Clevenger Distillation…… 21
- Moisture Content by Karl Fischer Method …… 21
- Absolute Density by Pycnometry …… 22

Tg by Differential Scanning Calorimetry (DSC) ..... 22
Molecular Void Size by Positron Annihilation Lifetime Spectroscopy (PALS)..... 22
Oxidation by Gas Chromatography ..... 23
Chapter 4: Results and Discussion ..... 25
Viscosity of Infeed Material..... 25
Infeed Emulsion Size and Reconstituted Powder Emulsion Particle Size..... 26
Volatile Retention..... 28
Particle Size of Spray Dried Powders..... 29
Absolute Density..... 30
Moisture Content..... 32
Glass Transition..... 33
Size of Molecular Voids..... 34
Orange Oil Oxidation..... 36
Chapter 5: Conclusions ..... 43
Chapter 6: Future Research ..... 45
Bibliography ..... 46
Chapter 7: Appendices..... 48
Appendix 1 (Chapter 4)..... 48
Unloaded and loaded infeed viscosity..... 48
Appendix 2 (Chapter 4)..... 49
Infeed emulsion size and reconstituted powder particle size..... 49
Appendix 3 (Chapter 4)..... 50
Volatile retention of spray dried orange oil by Clevenger distillation..... 50
Appendix 4 (Chapter 4)..... 51
Particle size of unloaded and loaded spray dried powders..... 51
Appendix 5 (Chapter 4)..... 52
Absolute density of unloaded and loaded spray dried powders stored at water activity of 0.11, 0.33 and 0.53 aw..... 52
Appendix 6 (Chapter 4)..... 54
Moisture content of unloaded and loaded spray dried powders stored at water activity of 0.11, 0.33 and 0.53 aw..... 54
Appendix 7 (Chapter 4)..... 56
Tg of unloaded and loaded spray dried powders stored at water activity of 0.11, 0.33 and 0.53 aw..... 56
Appendix 8 (Chapter 4)..... 62
Size of molecular voids of unloaded and loaded spray dried powders stored at water activity of 0.11, 0.33 and 0.53 aw..... 62
Appendix 9 (Chapter 4)..... 68
Oxidation of spray dried orange oil stored at water activity of 0.11, 0.33 and 0.53 aw..... 68

# List of Tables

## Chapter 3

Table 3.1: Unloaded spray dryer infeed formulation…… 18
Table 3.2: Loaded orange oil spray dryer infeed emulsion formulation…… 18

## Chapter 4

Table 4.1: The influence of carrier wall material on the infeed emulsion particle size and the particle size of the reconstituted powder emulsion…… 27
Table 4.2: The effect of carrier type and water activity on the absolute density of the unloaded (no orange oil) spray dried powder stored at ambient temperature (water activity of 0.11, 0.33 and 0.53 aw)…… 30
Table 4.3: The effect of carrier type and water activity on the absolute density of the loaded spray dried orange oil stored at ambient temperature (water activity of 0.11, 0.33 and 0.53 aw)…… 30
Table 4.4: The effect of carrier type and water activity on the average moisture content of the unloaded (no orange oil) powders and loaded spray dried orange oil stored at stored at ambient temperature (water activity of 0.11, 0.33 and 0.53 aw)…… 31
Table 4.5: The effect of carrier type and water activity on the glass transition of the unloaded (no orange oil) spray dried powder stored at ambient temperature (water activity of 0.11, 0.33 and 0.53 aw)..…….. 32
Table 4.6: The effect of carrier type and water activity on the glass transition of the loaded spray dried orange oil stored at 20°C (water activity of 0.11, 0.33 and 0.53 aw)……... 33
Table 4.7: The effect of carrier type and water activity on the size of molecular void of unloaded and loaded spray dried orange oil powders measured by PALS at ambient temperature…..…… 34

## Chapter 7

Table 7.1: Unloaded infeed viscosity……
Table 7.2: Loaded infeed orange oil emulsion viscosity…… 48
Table 7.3: Infeed orange oil emulsion size…….. 48
Table 7.4: Reconstituted powder particle size…… 49
Table 7.5: Volatile retention of spray dried orange oil…… 49
Table 7.6: Particle size of unloaded spray dried powder…… 50
Table 7.7: Particle size of loaded spray dried orange oil…… 51
Table 7.8: Moisture content of unloaded spray dried powder stored at 0.11 aw…… 51
Table 7.9: Moisture content of unloaded spray dried powder stored at 0.33 aw…… 52
Table 7.10: Moisture content of unloaded spray dried powder stored at 0.53 aw….. 52
Table 7.11: Moisture content of loaded spray dried orange oil stored at 0.11 aw….. 52
Table 7.12: Moisture content of loaded spray dried orange oil stored at 0.33 aw….. 52
Table 7.13: Moisture content of loaded spray dried orange oil stored at 0.53 aw….. 53
Table 7.14: Density of unloaded spray dried powder stored at 0.11 aw……. 54

Table 7.15: Density of unloaded spray dried powder stored at 0.33 aw…… 54
Table 7.16: Density of unloaded spray dried powder stored at 0.53 aw……..... 54
Table 7.17: Density of loaded spray dried orange oil stored at 0.11 aw…..... 54
Table 7.18: Density of loaded spray dried orange oil stored at 0.33 aw…… 55
Table 7.19: Density of loaded spray dried orange oil stored at 0.53 aw…… 55
Table 7.20: Tg of unloaded spray dried powders stored at water activity of 0.11 aw. 56
Table 7.21: Tg of unloaded spray dried powders stored at water activity of 0.33 aw. 57
Table 7.22: Tg of unloaded spray dried powders stored at water activity of 0.53 aw. 58
Table 7.23: Tg of loaded spray dried powders stored at water activity of 0.11 aw…. 59
Table 7.24: Tg of loaded spray dried powders stored at water activity of 0.33 aw…. 60
Table 7.25: Tg of loaded spray dried powders stored at water activity of 0.53 aw…. 61
Table 7.26: Size of molecular voids of unloaded spray dried powders stored at water activity of 0.11 aw…… 62
Table 7.27: Size of molecular voids of unloaded spray dried powders stored at water activity of 0.33 aw…… 63
Table 7.28: Size of molecular voids of unloaded spray dried powders stored at water activity of 0.53 aw…… 64
Table 7.29: Size of molecular voids of loaded spray dried powders stored at water activity of 0.11 aw…… 65
Table 7.30: Size of molecular voids of loaded spray dried powders stored at water activity of 0.33 aw…… 66
Table 7.31: Size of molecular voids of loaded spray dried powders stored at water activity of 0.53 aw…… 67
Table 7.32: Oxidation of spray dried orange oil stored at water activity of 0.11 aw over 4 weeks…… 68
Table 7.33: Oxidation of spray dried orange oil stored at water activity of 0.33 aw over 4 weeks…… 68
Table 7.34: Oxidation of spray dried orange oil stored at water activity of 0.53 aw over 4 weeks…… 69

# List of Figures

## Chapter 1

Figure 1.1: Depiction of an encapsulated particle…….. 2
Figure 1.2: Characteristics and factors affecting the stability of encapsulated flavors 4
Figure 1.3: Rate of physiochemical changes of encapsulation systems as a function of water activity at a constant temperature…….. 5
Figure 1.4: Rate of physiochemical changes of encapsulation systems as a function of temperature…….. 8
Figure 1.5: Second-order glass transition as seen by a sigmodal step change in heat capacity, $\Delta C_p$, that occurs over the glass transition, $T_g$…… 9

## Chapter 4

Figure 4.1: The effect of carrier wall material on the infeed viscosity of the unloaded (no orange oil) and loaded orange oil samples with 35% solids and 25% orange oil load measured at 22°C using the Brookfield H1 spindle……. 25
Figure 4.2: The effect of carrier wall material on percent oil retention of the loaded spray dried orange oil as measured by Clevenger distillation…… 28
Figure 4.3: The influence of the carrier wall material on the particle size of unloaded (no orange oil) containing powders and loaded spray dried oil powders..... 29
Figure 4.4: A. The effect of maltodextrin carrier wall material on the generation of mg of Limonene Oxide per g of Limonene over 4 weeks of storage at ambient temperature and 0.33 aw B. The effect of maltodextrin carrier wall material on the rate of orange oil oxidation (generation of mg of Limonene Oxide per g of Limonene per week) at ambient temperature and 0.33 aw…… 36
Figure 4.5: A. The effect of carrier wall blends on the generation of mg of Limonene Oxide per g of Limonene over 4 weeks of storage at ambient temperature and 0.33 aw B. The effect of carrier wall blends on the rate of orange oil oxidation (generation of mg of Limonene Oxide per g of Limonene per week) at ambient temperature and 0.33 aw..... 36
Figure 4.6: A. The effect of water activity on the rate of orange oil oxidation (generation of mg of Limonene Oxide per g of Limonene per week) of Maltrin 150 carrier wall material stored at ambient temperature B. The influence of water activity on the rate of oxidation of spray dried orange oil with Maltrin 150 as the carrier wall material at ambient temperature…. 37
Figure 4.7: A. The effect of water activity on the rate of orange oil oxidation (generation of mg of Limonene Oxide per g of Limonene per week) of 90% Maltrin 150 and 10% Gum Acacia carrier wall material stored at ambient temperature B. The influence of water activity on the rate of oxidation of spray dried orange oil with 90% Maltrin 150 and 10% Gum Acacia as the carrier material stored at ambient temperature…… 38

Figure 4.8: A. The effect of water activity on the rate of orange oil oxidation (generation of mg of Limonene Oxide per g of Limonene per week) of 90% Maltrin 150 and 10% HiCAP 100 carrier wall material stored at ambient temperature B. The influence of water activity on the rate of oxidation of spray dried orange oil with 90% Maltrin 150 and 10% HiCAP 100 as the carrier wall material at ambient temperature…… 38

# Chapter 1: Literature Review

## Introduction

Food flavor is a driving food sensory attribute that often dictates the overall acceptance of food products. Unfortunately, during handling, processing, and storage, flavors fall subject to loss and degradation. Flavors can migrate out of the food and be lost to their environment or they can interact with other food ingredients and packaging material leading to isomerization and oxidation thereby affecting food acceptability. Early flavor research took a materials science approach towards protecting sensitive food ingredients such as flavors by using encapsulation technology. Encapsulation is a process by which flavor molecules are dispersed as micrometer particles in a larger, protective capsule. Many industries such as pharmaceutical, heath, paper and cosmetics, have utilized encapsulation technology to protect sensitive ingredients (Risch and others 1995).

## Encapsulation

There are many methods for encapsulation including: spray drying, spray chilling/cooling, coacervation, extrusion, fluidized coating, liposome entrapment and molecular inclusion (Gouin, 2004). Spray drying was the first process used to encapsulate flavorings and it is the choice methodology for encapsulation due to the wide availability of equipment, low process cost, ease of use, variety of possible carrier solids, good volatile retention, and adequate shelf life of the final dry powder (Risch and others 1988; Reineccius 2004).

To encapsulate flavors via spray drying, a carrier or wall material is dissolved in water, a flavor is added to the solution, and an emulsion is formed. The emulsification

process allows for the flavor to be entrapped by the carrier matrix leading to an aqueous emulsion system of flavor. Once an emulsion has formed, the solution is atomized (two fluid atomizer pressure spray or centrifugal wheel atomization) into a stream of hot air, which rapidly dries the microcapsules trapping the flavor inside dry particles (Figure 1.1) and results in a free-flowing powder (Risch and others 1988).

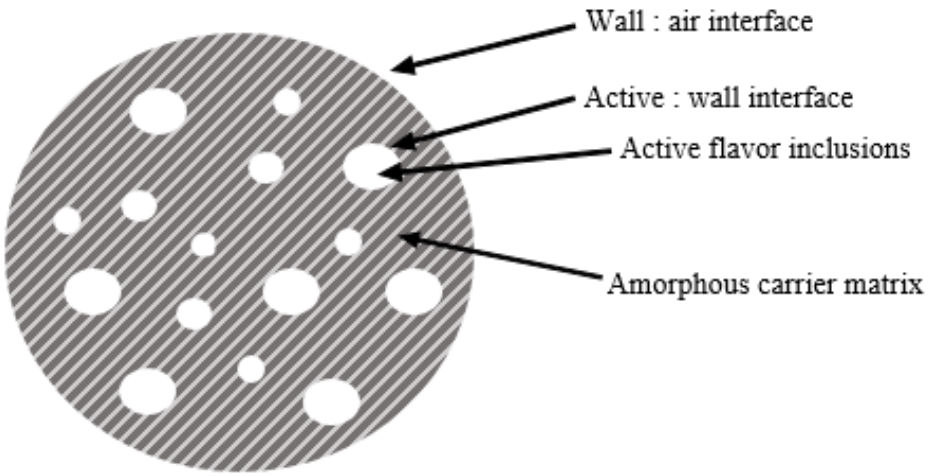



Figure 1.1 Illustration of a spray dried encapsulated powder particle Figure adapted from (Reineccius and Yan 2016).

**Carrier Materials**

There is a wide variety of ingredients that can be used as encapsulation carrier material. Extensive research has gone into determining a carrier matrix that displays superior aroma retention and barrier properties for maximum shelf life. Attributes of a good carrier material include: emulsifying properties and film-forming properties, low viscosity, low hygroscopicity, high solids content in solution, and it is stable, cheap, and tasteless (Risch and others 1988). There are three classes of common carrier materials used for spray

drying: gums (i.e. gum acacia), mono- and disaccharides (i.e. maltodextrins and corn syrup solids) and chemically modified starch hydrolysates.

### *Choice of Carrier Material*

It is important that the choice of carrier material be carefully considered as it greatly influences flavor retention during the spray drying process an oxidation during subsequent storage until consumption (Buffo and others 2002). The choice of carrier affects many of the encapsulated powder's characteristics including: particle size and shape, absolute and bulk density, flowability, dispersibility, moisture content, appearance, flavor load, shelf-life, stability to caking, structural strength, and release properties (Reineccius 2004). There is not one single wall material that exhibits all of the properties of a perfect carrier. Because of this, blends of carbohydrates are used to improve the encapsulation properties of the carrier matrix.

## Factors Affecting the Stability of Encapsulated Material

Encapsulation can protect sensitive ingredients such as flavors, however, the protective effects of encapsulated materials are altered by changes in water content and temperature during processing, handling and storage. These environmental conditions significantly impact the physical state of the carrier material resulting in measurable changes in the glass transition, molecular mobility, size of molecular voids, and number of molecular voids in the encapsulation matrix (Figure 1.2) (Townrow and others 2007; Townrow and others 2010; Kilburn and others 2004; Ubbink and others 2007; Ubbink 2009; Ubbink 2013). Consequently, encapsulated ingredients such as flavors become subject to volatile migration and loss or oxidation.

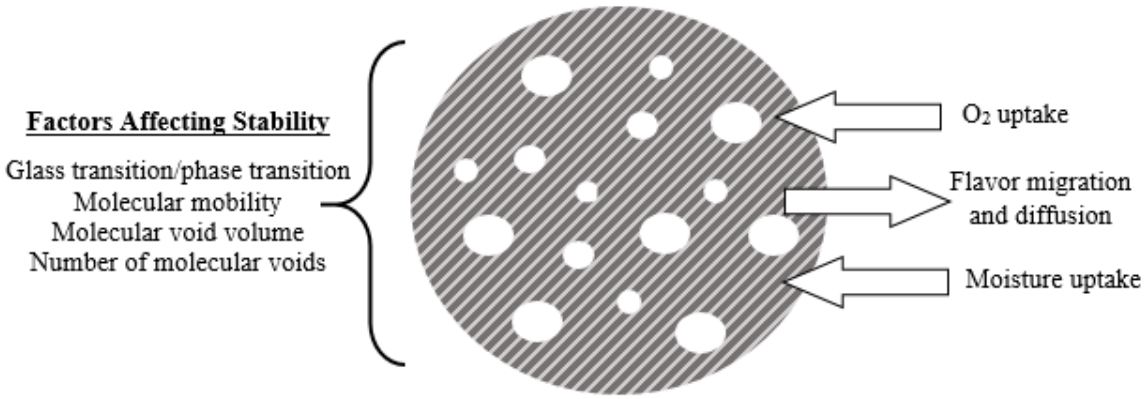



Figure 1.2 Characteristics of spray dried encapsulated flavors and factors affecting the stability of encapsulated flavors. Figure adapted from (Ubbink 2013).

## Phase Transitions

The sensory, physical and chemical properties of all food systems are controlled by the food's physical state. The physical state of a food changes when there is a phase transition or a change in physical state between a solid, liquid or gas. The physical state of a food system is dependent on temperature and water content. Phase transitions are also dependent on pressure however, since most food is transported, stored and consumed at atmospheric pressure, the influence of pressure on the physical state of food is negligible.

### *Temperature*

For most food systems, an increase in temperature yields an increase in the rate of chemical reactions and the same principle holds true for encapsulated flavor systems. The reason for this is that an increase in temperature results in an increase in the collision rate of molecules and when molecules collide, they chemically react. Not only can increases in temperature increase the rate of chemical reaction, but temperature can also change the physical state of food from the amorphous glassy state to the more permeable rubbery state.

***Water Content***

Water is a component of all food products and its presence will influence the physical properties, microbiological viability and growth, sensory properties, stability and phase behavior of foods. The amount of water in a food system is described by water activity and moisture content. While moisture content refers to the proportion of water to the amount of solids in the system, water activity, $a_w$, is the vapor pressure of water, *P food*, in equilibrium with a food, relative to that of the vapor pressure of water, *P* $H_2O$, at the same temperature (equation 1.1) (Labuza 1977).

$$a_w = \frac{P\ food}{P\ H2O} \qquad 1.1$$

In general, as the water activity of an encapsulation system increases the rate of physiochemical changes also increases as depicted in Figure 1.3 (Roos 2016).

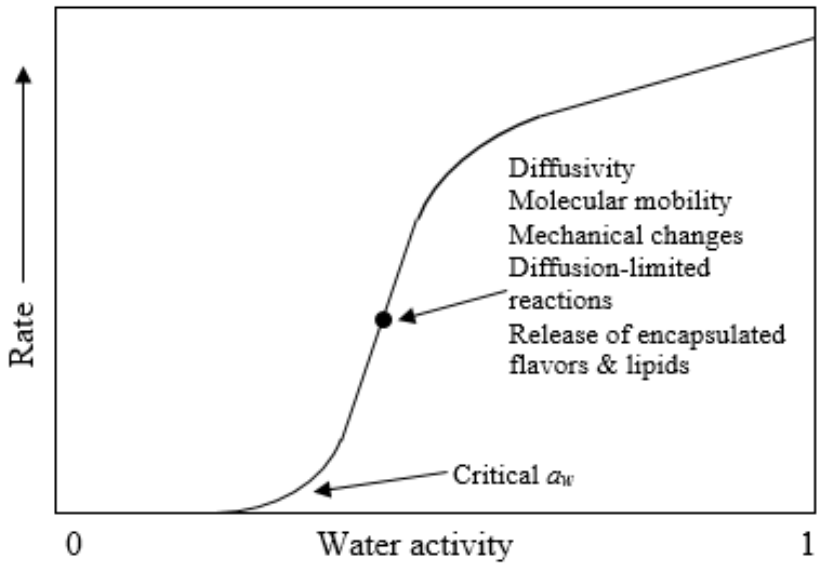



Figure 1.3 Rate of physiochemical changes of encapsulation systems as a function of water activity at a constant temperature. Figure adapted from (Roos 2016).

## Moisture Sorption Isotherms

Moisture sorption isotherms are used to illustrate and predict the physical state of foods relating the amount of moisture absorbed as a function of relative vapor pressure, or water activity, at a constant temperature. There are two different models that are widely used to predict moisture sorption: the Brunauer, Emmet, and Teller (BET) isotherm and the Guggenheim-Anderson-de Boer (GAB) isotherm.

### *BET Model*

The Brunauer, Emmet, and Teller (BET) isotherm is used to find the monolayer of a food matrix. The monolayer is a value describing the amount of water needed to form a one molecule thick layer of water on the food matrix surface. The model equation is given by equation 1.2 where *m* is the water content (g/100 g of solids), $m_m$ is the monolayer value, and *K* is a constant.

$$\frac{m}{m_m} = \frac{a_w}{(1-a_w)[1+(K-1)a_w]} \qquad 1.2$$

The BET model has some limitations as the equation only applies to food matrices over a narrow water activity range (Rha 1975).

### *GAB Model*

The Guggenheim-Anderson-de Boer (GAB) isotherm describes the sorption of water by a polymer matrix and can also be used to determine the monolayer value. The model equation is given by equation 1.3 with identical parameters to the BET model equation with the exception of the addition of *C*, a constant.

$$\frac{m}{m_m} = \frac{K\prime C a_w}{(1-C a_w)[1+(K\prime-1)C a_w]} \quad 1.3$$

The GAB model is the most widely used moisture sorption isotherm because fits experimental data over a wide range of water activities as the model assumes that multilayer water is not as strongly bound as the monolayer. Researchers can create GAB moisture sorption isotherms using experimental data to predict the physical state of food products as a function of $a_w$.

**Physical State Characterization of Amorphous Materials**

Carrier wall materials in encapsulated systems exist as amorphous polymers. In contrast to a crystalline, ordered molecular structure, an amorphous material is in a state of non-equilibrium and has a disordered molecular structure. The field of materials science identified the two physical states of amorphous materials as: a viscoelastic, rubbery state and a solid, glassy state. At low temperatures, amorphous materials are solid and glassy where there is little to no molecular movement. As the temperature or moisture content increases, the amorphous material approaches the glass transition temperature, $T_g$. Above the $T_g$ amorphous materials are in the rubbery state and their molecular movement increases. $T_g$ is the temperature that separates a food system from its rubbery and glassy states marking the critical point of stability. Moisture sorption isotherms are used to illustrate the glassy and rubbery states as these two different physical states are a function of temperature (Figure 1.4).

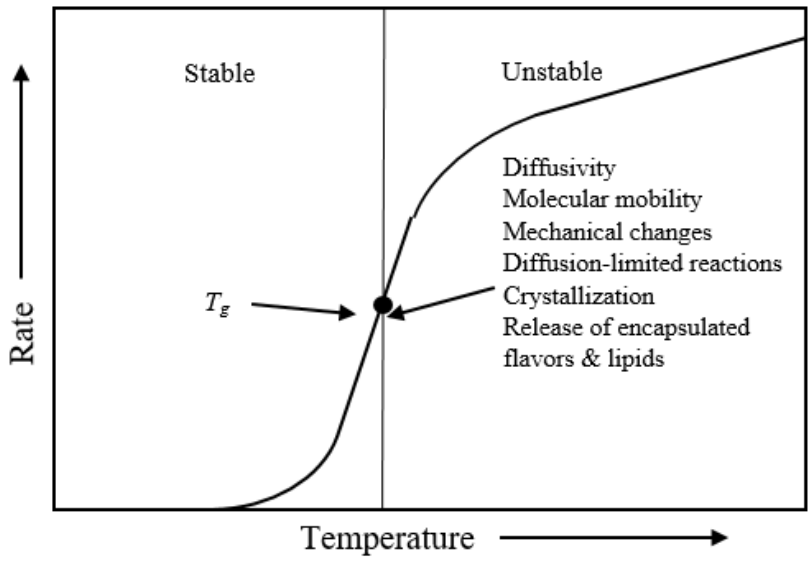



Figure 1.4 Rate of physiochemical changes of encapsulation systems as a function of temperature. Adapted from (Roos 2016).

**Determination of Glass Transition Temperature**

As the physical state of the carrier matrix changes at the $T_g$, so do the associated thermodynamic properties of the physical state which include enthalpy, entropy, and volume. The $T_g$ can be experimentally determined by calorimetric measurements where a definitive change in heat capacity indicates a $T_g$. Differential scanning calorimetry (DSC) is a common technique used to determine the phase transition of amorphous materials by detecting endothermic and exothermic reactions that occur as a function of temperature. DSC measures the change in enthalpy ($\Delta H$) at first-order transition temperatures, as well as changes in heat capacity ($\Delta C_p$) at second-order transition temperatures. These second-order glass transitions typically occur over a temperature range of 10-30°C (Roos and Drusch 2015). Thermographs depict first-order transitions as peaks in which latent heat

from melting and crystallization can be calculated. Second-order glass transitions are shown as sigmodal step changes (Figure 1.5).

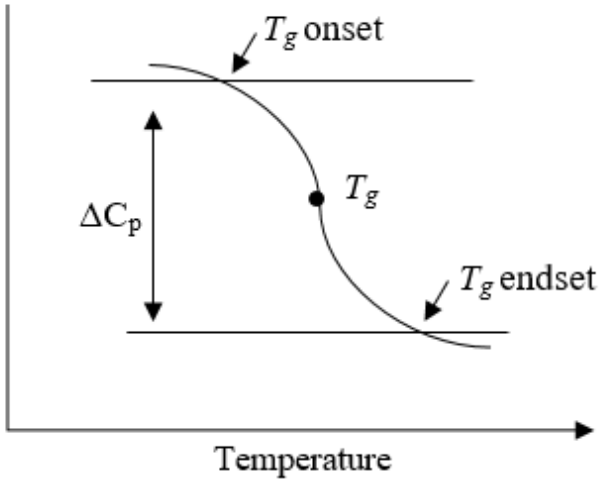



Figure 1.5 Second-order glass transition as seen by a sigmodal step change in heat capacity, $\Delta C_p$, that occurs over the glass transition, $T_g$. Adapted from (Roos 2016).

**Molecular Mobility**

Molecular mobility is the change in location of a molecule in relation to other molecules in a matrix as well as intermolecular conformational changes. As matrices approach the glass transition, molecular mobility becomes evident. As stated previously, below the $T_g$ there is little to no molecular mobility and the matrix is said to be stable as chemical reactions occur very slowly. Above the $T_g$, more molecular mobility is observed as the viscosity, flow, and rate of chemical reactions increase. Molecular mobility is a contributing factor to the diffusion of volatile compounds out of the encapsulation system as well as the migration of small molecules such as water or oxygen into the encapsulation matrix thereby impacting flavor stability.

## Glass Transition Theories

The free volume theory and the kinetic theory have been used to describe the influence of the glass transition on the stability of encapsulated systems.

### *Free Volume Theory*

The free volume theory, states that molecular voids, or free volume, must be present in order for molecular motion to occur. The theory assumes that at the glass transition temperature there is a change in the thermal expansion coefficient, therefore a change in the fractional free volume, *f*, above the $T_g$. The free volume theory is described by equation 1.4 where $f_g$ is the fractional free volume at $T_g$ and $\alpha_f$ is the thermal expansion coefficient (Roos and Drusch 2015).

$$f = f_g + \alpha_f (T - T_g) \tag{1.4}$$

It is important to note that the fractional free volume is also related to the specific free volume, $v_f$,, and the macroscopic volume, v (Equation 1.5). Furthermore, $v_0$ is the volume occupied by molecules (Equation 1.6) (Roos and Drusch 2015).

$$f = \frac{v_f}{v} \tag{1.5}$$

$$v_f = v - v_0 \tag{1.6}$$

According to the free volume theory an increase in $T_g$ results in an increase in free volume which is directly related to the absolute density of the encapsulated system.

***Kinetic Theory***

The kinetic theory explains the time-dependency of $T_g$ and the associated molecular relaxations that occur over a temperature range (Roos and Drusch 2015). As previously stated, in the glassy state there is little to no molecular movement, if this statement is true then the molecular voids present in the glassy state will remain unchanged in number, size or positon. When the physical state of the matrix changes, and the system passes through the $T_g$ there is a change in the number, size or positon of the molecular voids. Equation 1.7 is used to describe the equilibrium number of molecular voids ($N'_h$). The theory assumes that a matrix has voids with a molar volume, $v_h$, or that molecular voids do not exist leading to a matrix with excess molar energy, $\varepsilon_h$. In equation 1.7, $N_0$ is the number of moles of repeating matrix units, $v_0$ molar volume of each repeating matrix unit, and $\varepsilon_j$ is the associated activation energy for the appearance and disappearance of molecular voids (Roos and Drusch 2015).

$$N'_h = N_0 \left(\frac{v_0}{v_h}\right) e^{-\varepsilon_j/RT} \qquad 1.7$$

The relaxation time or disappearance of molecular voids, $\tau_h$, is described by equation 1.8 where $h$ is the Planck constant, $k$ is the Boltzmann constant, $Q^h$ is the partition function of molecular voids and $Q^{\Xi}$ represents the activated state.

$$\tau_h = \frac{h}{kT}\frac{Q^h}{Q\Xi} e^{\varepsilon_j/RT} \qquad 1.8$$

Researchers can experimentally determine the volume ($v_0/v_h$) of a matrix by correlating experimental data of free volume measured by pycnometry and molecular void size measured by positron annihilation lifetime spectroscopy (PALS).

### Influence of Carrier Molecular Weight on $T_g$

Researchers Fox and Flory investigated the influence of carrier material molecular weight on $T_g$. They determined that $T_g$ increases as the molecular weight of the carrier material increases. From these results they developed the Fox and Flory Equation, equation 1.9, to predict the influence of molecular weight on $T_g$. In the equation, $T_g\infty$ is the maximum glass transition temperature for a theoretical infinite molecular weight, K is the free volume constant and $M_n$ is the number average molecular weight (Fox and Flory 1950).

$$T_g = T_g(\infty) - \frac{K}{M_n} \quad 1.9$$

#### *Packing Enhancers*

The free volume and density of a polymer matrix is also related to the molecular weight of the carrier material. It has been well documented that incorporating low molecular weight sugars, such as maltose or glycerol, leads to increased volatile retention and oxidative stability (Bangs and Reineccius 1982; Subramaniam and others 2013). It has been proposed that the smaller molecules reduce mobility of small permeates such as volatiles, oxygen, and water, through the carbohydrate chain by increasing molecular packing and matrix density leading to smaller void space (Kilburn and others 2005). These low molecular weight carrier materials have been referred to as packing enhancers as they decrease the size of molecular voids due to more efficient hydrogen bonding with neighboring carbohydrate molecules (Townrow and others 2010; Roussenova and others 2010).

### *Plasticization and Antiplasticization*

Smaller molecular weight carrier materials have also been referred to as plasticizers. Plasticizers decrease the glass transition temperature and are used to make the carbohydrate matrix more ductile. Antiplasicization occurs when the glass transition temperature increases and the carbohydrate matrix becomes more rigid.

Water can act as a plasticizer or an antiplasticzer. Townrow et al. suggests that at low water contents in the glassy state, water acts by filling free volume holes between the amorphous carbohydrate wall molecules. This hole filling mechanism is also known as antiplasticization. As the water content increases in the glassy state, the void volume increases and specific volume decreases due to the plasticizing effect of water allowing more molecular mobility and for water molecules to more closely associate with the carbohydrate molecules (Townrow and others 2010).

## Positron Annihilation Lifetime Spectroscopy

Researchers have used free volume to predict molecular mobility (Kilburn and others 2005; Ubbink 2009; Townrow and others 2007; Townrow and others 2010; Kilburn and others 2004). The most accurate method for measuring the amount of free volume is by using positron annihilation lifetime spectroscopy (PALS). PALS has been used to investigate the influence of temperature, water activity and plasticizers on the nanostructure of glassy carbohydrate matrices (Townrow and others 2010; Roussenova and others 2010; Kilburn and others 2004; Ubbink and others 2007). PALS measures the hole size between molecules in the size range of the van der Waals radius of oxygen, around 0.1 nm, making this the choice technique for oxygen permeability in food polymers

(Reineccius and Yan 2016). PALS determines the intermolecular void size by using *ortho*-positronium (o-Ps) from a radioactive source, such as $Na^{22}$. The $Na^{22}$ isotope probe bombards the sample with positrons leading to ionizing collisions with sample electrons causing them to exist in two different spin states: an antiparallel spin state, *para*-positronium (*p*-Ps) or a parallel triplet spin state, *ortho*-positronium (*o*-Ps). The average decay of the *ortho*-positrons is measured and is directly related to the intermolecular free volume void size (Siegel 1980). The lifetime of *ortho*-positron decay is described by equation 1.10 where R is the average free volume void radius, $R_0=R+\Delta R$, and $\Delta R=0.166$ nm (Roos and Drusch 2015).

$$\tau_{o-Ps} = \frac{1}{2}\left[1 - \left(\frac{R}{R+R_0}\right) + \frac{1}{2\pi} sin\left(\frac{2\pi R}{R+R_0}\right)\right]^{-1} \quad 1.10$$

Kilburn et al. was the first to study the nanostructure of amorphous carbohydrates using PALS (Kilburn and others 2004). Combining this information with thermodynamic analysis, Kilburn et al. determined that glassy carbohydrate void volume and matrix density increases with increasing water content which impacts carbohydrate hydrogen bonds allowing for rearrangements of the free volume (Kilburn and others 2004). Kilburn et al. proposed that water occupies the intermolecular voids between the polymer chains below the $T_g$ (Kilburn and others 2004). As the system approaches the glass transition temperature, the void space begins to increase (Kilburn and others 2004).

**Diffusion**

Encapsulation by spray drying yields an amorphous powder where the carbohydrate wall material is solid, has limited mobility and a high viscosity, however, diffusion still occurs (Reineccius and Yan 2016). Diffusion is the movement of molecules from higher

concentration to lower concentration as stated by the thermodynamic theory, entropy. Flavor loss is attributed to the diffusion of aroma compounds through the wall material or the loss of integrity of the wall material. Ignoring interactions between the carrier wall material and flavor components, the glass transition properties of carrier materials dictates the inherent diffusional loss of volatile components. The rate of diffusion ($D_{rate}$) is controlled by the molecular volume of the molecule (*MV)*, free volume of the carrier matrix *(FreeVol)*, and the molecular mobility of the carrier material *(MM)*. The relationship is described by equation 1.11 where *Sol* is the solubility of the molecule in the wall material and *VP* = vapor pressure (Reineccius and Yan 2016).

$$D_{rate} \propto \frac{Sol \times MM \times FreeVol \times VP}{MV} \qquad 1.11$$

If the molecular volume of the molecule, free volume of the carrier matrix, or molecular mobility of the carrier material increases as a result of an increase in $T_g$ the diffusion rate will also increase.

**Flavor Oxidation**

Diffusion not only contributes to flavor losses, but it also allows for the migration of oxygen and moisture throughout the microcapsule contributing to oxidation (Reineccius and Yan 2016; Orlien and others 2000). It is well documented that slight changes in free volume affect oxygen diffusivity and subsequent oxidation of bioactive compounds encapsulated by glassy carbohydrates thereby affecting of the shelf life (Drusch and others 2009; Reineccius 2004; Drusch and others 2012; Ubbink 2013).

# Chapter 2: Objective & Hypotheses

## Objective

The objective of this Master's thesis project was to determine whether molecular mobility and/or free volume influences the oxidative stability of spray dried orange oil.

## Hypotheses

1. Spray drying carrier systems that are formulated to provide the lowest free volume will provide the greatest protection to spray dried orange oil samples.
2. Spray drying carrier systems that are formulated to provide the lowest molecular mobility (measured by glass transition temperature) will provide the greatest protection to spray dried orange oil samples.
3. There is an ideal balance between molecular mobility and molecular free volume that provides the greatest protection against the oxidation of spray dried orange oil.

# Chapter 3: Materials & Methods

## Chemicals

Gas chromatographic (GC) grade acetone (Sigma Aldrich Inc., St. Louis, MO, USA) was used for gas chromatographic analysis. 4-heptamone (Sigma Aldrich Inc., St. Louis, MO, USA) was used as the internal standard for all GC analysis. Anhydrous methanol (Avantor, Center Valley, PA, USA), anhydrous sodium sulfate (Fisher Scientific, Fair Lawn, NJ, USA), and the chemicals comprising the pyridine free reagents kit (Photovolt Instruments Inc., Minneapolis, MN, USA) for the Karl Fischer titration system were used for Karl Fischer moisture analysis. Lithium chloride, magnesium chloride hexahydrate, and magnesium nitrate hexahydrate salts were used to make saturated salt solutions for the adjustment of sample relative humidity (Sigma Aldrich).

## Preparation of Orange Oil Emulsion

Orange oil (Firmenich, Princeton, NJ, USA) was used as the encapsulation load material. Maltrin 40, Maltrin 100, Maltrin 150, Maltrin 180, Maltrin 250, (various dextrose equivalent maltodextrins) (Grain Processing Corporation, Muscatine, IA, USA), Gum acacia (TIC Gums, White Marsh, MD, USA) and HI-CAP®100, (octenyl succinic anhydride, OSAn, substituted modified starch) (Ingredion, Westchester, IL, USA) were used as carrier materials. The formulas used to produce unloaded (no orange oil) emulsions and the loaded (orange oil containing) emulsions are found in Table 1.1 and Table 1.2.

The carrier material for each formula was dissolved in ca. 20 °C deionized water and was mixed using a high shear mixer (Greerco Corp., Hudson, NH, USA) until complete dissolution. Each carrier material solution was allowed to hydrate overnight at ambient

temperature. Immediately before spray drying, orange oil was added at 25% of the solids content to each of the loaded orange oil formulations and mixed using a high shear mixer (Greerco Corp., Hudson, NH, USA) for 2 min. followed by homogenization using a GEA Niro-soavi PANDA 2K homogenizer (GEA, Parma, Italy) at 160 atm.

Table 1.1 Unloaded spray dryer infeed formulations

| Composition | Water (g) | Maltodextrin (g) | Gum Acacia (g) | HI-CAP®100 (g) | Orange oil (g) |
|---|---|---|---|---|---|
| Maltrin 40 | 267 | 144 | x | x | x |
| Maltrin 100 | 267 | 144 | x | x | x |
| Maltrin 150 | 267 | 144 | x | x | x |
| Maltrin 180 | 267 | 144 | x | x | x |
| Maltrin 250 | 267 | 144 | x | x | x |
| 90% Maltrin 150 + 10% Gum Acacia (GA) | 267 | 129.6 | 14.4 | x | x |
| 80% DE 15 + 20% Gum Acacia (GA) | 267 | 115.2 | 28.8 | x | x |
| 90% Maltrin 150 +10% Modified Starch (MS) | 267 | 129.6 | x | 14.4 | x |
| 80% Maltrin 150 + 20% Modified Starch (MS) | 267 | 115.2 | x | 28.8 | x |

Table 1.2 Loaded orange oil spray dryer infeed emulsion formulations

| Composition | Water (g) | Maltodextrin (g) | Gum Acacia (g) | HI-CAP®100 (g) | Orange oil (g) |
|---|---|---|---|---|---|
| Maltrin 40 | 400.5 | 162 | x | x | 54 |
| Maltrin 100 | 400.5 | 162 | x | x | 54 |
| Maltrin 150 | 400.5 | 162 | x | x | 54 |
| Maltrin 180 | 400.5 | 162 | x | x | 54 |
| Maltrin 250 | 400.5 | 162 | x | x | 54 |
| 90% Maltrin 150 + 10% Gum Acacia (GA) | 400.5 | 145.8 | 8.64 | x | 54 |
| 80% DE 15 + 20% Gum Acacia (GA) | 400.5 | 129.6 | 17.28 | x | 54 |
| 90% Maltrin 150 +10% Modified Starch (MS) | 400.5 | 145.8 | x | 8.64 | 54 |
| 80% Maltrin 150 + 20% Modified Starch (MS) | 400.5 | 129.6 | x | 17.28 | 54 |

**Spray Dryer Infeed Emulsion Viscosity**

Immediately after homogenization, a Dial Reading Brookfield Viscometer (Model RV: Brookfield Ametek, Middleboro, MA, USA) was used to measure the viscosity of each emulsion at 23°C. The viscosity was determined using the standard manual procedure using the H1 spindle at 10 rpm. To convert the viscometer dial reading to a viscosity value in units of centipoise, the reading noted on dial viscometer was multiplied by the appropriate factor for the viscometer model/spindle/speed combination from the Brookfield conversion tables.

**Spray Dryer Infeed Emulsion Particle Size**

Immediately after homogenization, the average emulsion size of the carrier/orange oil infeed emulsion was determined using a Horiba LA-960 Laser Particle Size Analyzer (HORIBA Scientific, Edison, NJ, USA). Approximately 50-500 μL of each emulsion was added to the instrument and the emulsion particle size results for each emulsion was reported as the mean size based on 95 measurements per run. Infeed emulsion size was analyzed in duplicate.

**Spray Drying**

During spray drying, the carrier/orange oil emulsion was continuously mixed using a stir plate and stir bar to help prevent phase separation of the orange oil. Spray drying was conducted using a Buchi Mini Spray Drier B-290 (BUCHI Corporation, New Castle, DE, USA). The spray drier operates using an integrated two-fluid nozzle (0.7 mm diameter) and a mass air flow of 473 l/h. The inlet operating temperature was 180°C the outlet

temperature was 80°C. The feed rate was ≈73 mL/min and varied to maintain the specified outlet temperature.

**Storage of Spray Dried Powders**

Desiccators were allowed to equilibrate at least three weeks prior to spray drying with water activities (aw) of 0.11, 0.33 and 0.52. Lithium chloride, magnesium chloride hexahydrate, and magnesium nitrate hexahydrate salts were used to achieve the desired water activities. Immediately after spray drying, approximately 10 g of each powder was placed in the differing aw desiccators to begin the storage study. The remaining loaded orange oil powders were stored in closed glass jars at -20°C to prevent oxidation while the unloaded powders were stored in glass jars at ambient temperature.

**Particle Size of Spray Dried Material**

To determine the average particle size of the spray dried powders, a Horiba LA-960 Laser Particle Size Analyzer (HORIBA Scientific, Edison, NJ, USA) was used. Approximately 0.5 g of each powder was added to the instrument at (Air pressure: 0.15 mPa, Feeder: 100% (Automatic), Refractive Index: 1.67) and the particle size was reported as the mean size based on 95 measurements per run. Particle size was analyzed in duplicate.

**Reconstituted Powder Emulsion Particle Size**

To determine if the emulsion size stayed the same after spray drying, 1.5 g of each loaded orange oil powder was rehydrated in 8.5 mL of deionized water and mixed. The reconstituted powder emulsion particle size was determined using a Horiba LA-960 Laser Particle Size Analyzer (HORIBA Scientific, Edison, NJ, USA). Approximately 500 μL of each reconstituted powder was added to the instrument and the emulsion particle size

results were reported as the mean size based on 95 measurements per run. Reconstituted powder particle size was analyzed in duplicate.

**Volatile Retention by Clevenger Distillation**

The total volatile retention of the spray dried orange oil material was determined by Clevenger Distillation. Spray dried orange oil powder (5 g) was dissolved in 200 mL of distilled water in a 500 mL round-bottom flask. Then, ca. 0.1 mL of vegetable oil was added to the flask as an antifoam agent and the Clevenger trap was connected to the sample flask and a water-cooled condenser was placed on top of the Clevenger trap. The heat source for distillation was adjusted so that approximately one drop of distillate is achieved every second or two. The distillation was carried out for 2 h, and the apparatus was allowed to cool to cool to ambient temperature and then the volume (mL) of distilled oil was read directly from the collection arm. The volume of oil was converted to mass by multiplying by the density of the oil (0.82-0.86 g/mL) as determined gravimetrically at 20°C (Merck and others 2000). The volatile oil or aroma retention during spray drying was calculated as follows: Volatile oil retention % = [(Measured oil content)/ (theoretical oil content)] X 100%

**Moisture Content by the Karl Fischer Method**

The moisture content of each of the unloaded and loaded orange oil powders stored at differing water activities (0.11, 0.33 and 0.53 aw) was determined by the Karl Fischer method using a Metrohm KF756 Aquatest CMA instrument (Photovolt Instruments Inc., Minneapolis, MN, USA). Approximately 0.3 g of each spray dried powder was weighed into 20-mL headspace vials. Approximately 10 g of anhydrous methanol was weighed into

the vial that contained the spray dried material and the vial was capped and allowed to equilibrate at 20°C overnight. Approximately 1 mL was injected into the Aquatest CMA instrument and the Aquatest output reading was used to calculate the moisture content on a dry basis according to the manual instructions. Methyl alcohol blanks were also measured to correct for residual moisture in the solvent. Moisture content analysis was measured in duplicate.

**Absolute Density by Nitrogen Pycnometry**

The density of the spray dried powders was determined by nitrogen pycnometry. The pycnometer was calibrated according to the manual instructions. To determine the specific volume, approximately 1.5 to 3 g of spray dried material was weighed into the sample cell of a Quantachrome Multipycnometer (Quantachrome Corporation, Boynton Beach, FL, USA). Using the standard calculation methodology, the density ($g/cm^3$) of each spray dried powder was determined. Density analyses were performed in duplicate.

**Tg by Differential Scanning Calorimetry (DSC)**

Calorimetric measurements were measured using a Perkin Elmer DSC 8000 system and software (PerkinElmer, Waltham, MD, USA). Approximately 35 mg of each spray dried powder was hermetically sealed in a 50 µL auto sampler aluminum sample pan (PerkinElmer, Waltham, MD, USA). An empty pan with pin was used as a reference. The software was programed to start at 0°C and heat 20°C/min to 135°C, cool -20°C/min to 0°C and hold at 0°C for 1 min. A second heat ramp to 135°C at 7°C/min was conducted and the glass transition of the spray dried orange oil was determined at the inflection point on the second heat ramp of the thermograph.

**Size of Molecular Voids by Positron Annihilation Lifetime Spectroscopy (PALS)**

Samples for PALS experiments were prepared by compaction of about 0.3 g of water-activity equilibrated powder into disks with a diameter of 10 mm and thickness of ~4 mm using a Carver laboratory tableting press at 1000 psi. The source of positrons, $Na^{22}$, was placed between a Kapton film (0.025 mm thick) on either side. Positrons penetrated into the sample, up to ~1 mm in depth. Large plastic scintillators (15 cm diameter, 15 cm length) are connected to high speed photomultipliers combined with timing electronics measure the lifetime of the positrons generated in the sample (Engbrecht and others 2013). Two detectors, one sensitive to 1270 keV γ-rays emitted from the $Na^{22}$ positron source and the other which detects γ-rays emitted from the annihilation of the positron with an electron from the sample. Two tablets of each sample were placed on either side of the positron source in a vacuum chamber of 100 mTorr (to eliminate interactions from the air) (Engbrecht and others 2013). All data was collected at ambient temperature. The decay time of *ortho*-positrons generated by each sample (measured in nanoseconds) is directly proportional to the size of molecular voids of the sample.

**Limonene Oxidation by Gas Chromatography (GC)**

The extent of orange oil oxidation was measured by gas chromatography. Approximately 1.5 g of each of the spray dried powders was dispersed in 8.5 ml of water and was mixed using a vortex mixer. One mL of the powder-water solution was transferred to another vial and 4 mL of 2.2% of 4-heptanone (internal standard) in acetone solution was added to the aqueous solution. After mixing and allowing the powder-water-internal standard and acetone solution to settle for 1 h, approximately 1 mL of the supernatant was transferred to 2 mL vials and loaded into a HP7673A automatic sampler (Hewlett-Packard, Wilmington,

DE). Using a HP5890 series II GC containing HP-5MS capillary column (30 m x 0.25 mm x 0.25 μm) (J&W Scientific, Folsom, CA) and a flame ionization detector (FID), 2 μL of each extract was automatically injected into the GC in split mode (20 to 1). The following operating conditions were used: hydrogen carrier gas at 55 kPa head pressure, 20 mL/min total carrier flow, 40°C initial oven temperature, ramping at 50 °C/min to a final temperature of 250°C, 220°C injection port temperature, 250°C FID temperature. Data collection and peak area integrations were performed. Limonene oxide was reported as the sum of its two major isomers. The oxidative stability of limonene was reported as mg of limonene oxide formed per g of limonene.

# Chapter 4: Results and Discussion

## Viscosity of Infeed Material

The viscosity of the infeed material influences the particle size of a spray dried material. The higher the viscosity the larger the particles. The larger the particles, the less surface area (as a percent of volume) there is for oxygen to permeate the particle and oxidize its contents. Theoretically, larger spray dried particles would lead to better flavor retention. As expected, the formulations containing maltodextrin as the sole carrier material showed a decrease in viscosity as the molecular weight of the carrier material decreased (Figure 4.1, Appendix 1) (Dokić Petar and others 2004). Since the solids content of the unloaded and loaded formulations were the same (35% solids), we attribute minor differences in the viscosity measurements between the unloaded and loaded formulations due to the fact that the portion of solids which was orange oil in the loaded formulations decreased the viscosity as orange oil is less viscous than water. Moreover, the oil could have acted as a lubricant for the spindle therefore decreasing the torque. The formulations that consisted of a blend of carrier wall material, as the ratio of maltodextrin decreased the viscosity increased as expected.

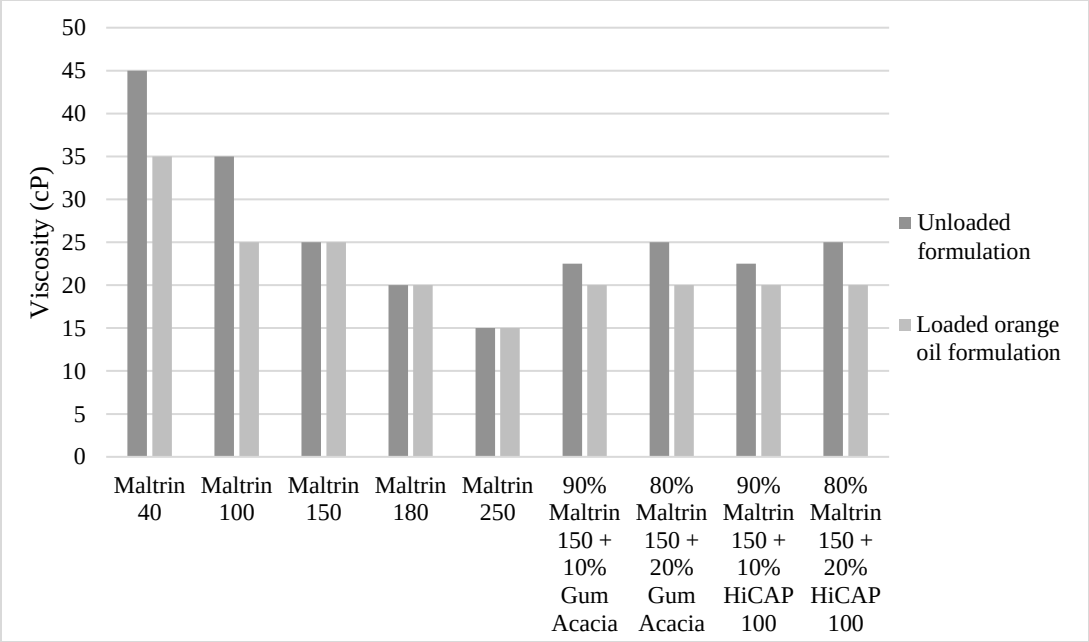



Figure 4.1: The effect of carrier wall material on the infeed viscosity of the unloaded (no orange oil) and loaded orange oil samples with 35% solids and 25% orange oil load measured at 22°C using the Brookfield H1 spindle.

**Infeed Emulsion Size and Reconstituted Powder Emulsion Particle Size**

Emulsion stability is a function of type of carrier wall material, ratio of carrier wall material to flavor material, solids content, temperature and extent of homogenization (Bangs and Reineccius 1982). Emulsion size indicates the emulsion stability of the carrier material while the reconstituted powder particle emulsion size is a reflection of the atomization of the spray drier. To maximize volatile retention and minimize oxidation during the spray drying process, the infeed emulsion size and the reconstituted powder emulsion particle size should be similar in size to prevent exposure of the active ingredient to high temperatures of spray drier.

In this study, the carrier wall material was the only variable affecting the stability of the emulsion (solids content 35%, oil load 25%). The large infeed emulsion size of the formulations containing maltodextrin as the sole carrier wall material indicates that

coalescence, or the joining of two smaller droplets to form one larger droplet, occurred immediately after homogenization (Table 4.1, Appendix 2). The coalescence of the maltodextrin emulsions is due to the fact that maltodextrin does not possess any emulsification properties while gum acacia and HiCAP® 100, an OSAn substituted modified starch, exhibit emulsifying properties (Dickinson 2009). The rehydrated spray dried powder containing maltodextrin as the sole carrier has significantly smaller values than the values obtained for the corresponding infeed emulsion size. Moreover, the particle size of the reconstituted powder was consistent among the different types of carrier wall materials. These results are attributed to the shearing action of the atomizer on the spray drier. We predict that even larger difference between the infeed emulsion size and the reconstituted powder particle size would be seen if a centrifugal wheel atomizer or a pressure nozzle were to be used for spray drying as these types of atomization create even more shear on the infeed emulsion thereby reducing their size.

Table 4.1: The influence of carrier wall material on the infeed emulsion particle size and the particle size of the reconstituted powder emulsion

| | Infeed Emulsion Size | | Reconstituted Powder Emulsion Particle Size | |
|---|---|---|---|---|
| Composition | Mean Particle Size (µm) | Standard Deviation (µm) | Mean Particle Size (µm) | Standard Deviation (µm) |
| Maltrin 40 | 39.4 | 0.00 | 2.15 | 0.01 |
| Maltrin 100 | 45.8 | 0.00 | 2.17 | 0.08 |
| Maltrin 150 | 44.8 | 0.00 | 2.43 | 0.34 |
| Maltrin 180 | 49.0 | 0.00 | 3.32 | 0.08 |
| Maltrin 250 | 47.6 | 0.00 | 2.21 | 0.16 |
| 90% Maltrin 150 + 10% Gum Acacia | 1.19 | 0.01 | 1.74 | 0.02 |
| 80% Maltrin 150 + 20% Gum Acacia | 0.47 | 0.05 | 1.42 | 0.17 |
| 90% Maltrin 150 + 10% HiCAP 100 | 1.15 | 0.02 | 1.90 | 0.52 |
| 80% Maltrin 150 + 20% HiCAP 100 | 0.78 | 0.01 | 1.72 | 0.79 |

**Volatile Retention**

Volatile retention is an indication of through put, and scale up feasibility. A low volatile retention indicates more loss of active ingredient to the environment during processing and before storage or transportation of the final powdered product.

Consistent with previous studies, the carrier systems containing an emulsifier displayed superior oil retention during spray drying compared to the carrier wall material formulations that only contained maltodextrin of various dextrose equivalence (Figure 4.2, Appendix 3) (Reineccius 2004). As expected, we observed a correlation between emulsion particle size and volatile retention. As the infeed emulsion particle size increased volatile retention decreased. We attribute the decrease in volatile retention to the high shear from atomization of the more coarse emulsions which exposes the volatile components to evaporation during drying (Soottitantawat and others 2003). Volatile retention is dependent on the ratio of carrier wall material to flavor material (held constant), solids content (held constant), type of carrier wall material and viscosity. Therefore, it is not concerning that the formulations containing maltodextrin as the sole carrier wall material had a much lower flavor retention. Had the infeed material been homogenized and directly fed into the spray dryer to limit coalescence, perhaps the volatile retention would have increased due to the smaller infeed emulsion size (Risch and others 1988). Moreover, the solids content of the infeed material could have been increased with would have also increased the viscosity of the infeed emulsions and resulted in better volatile retention.

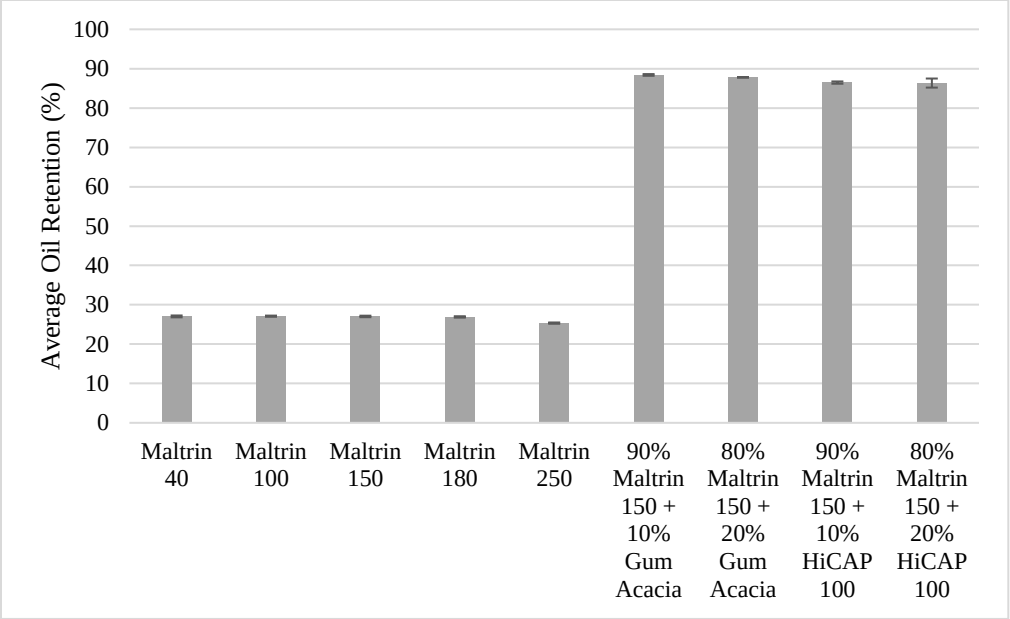



Figure 4.2: The effect of carrier wall material on percent oil retention of the loaded spray dried orange oil as measured by Clevenger distillation

**Particle Size of Spray Dried Powders**

The larger the particle size, the less surface area as a percent of volume there is for oxygen to permeate the particle and oxidize its contents. Usually larger spray dried particles lead to better flavor retention but there are many factors that contribute to the stability of spray dried materials. The particle size of the unloaded powders were comparable to the loaded orange oil containing powders however, there was some variability comparing the unloaded particle size to the loaded spray dried orange oil particle size (Figure 4.3, Appendix 4). The particle size of spray dried powders is dictated by the dryer design and operating conditions such as type and operating parameters of atomization, infeed solids content and drying air temperatures (Reineccius 2004). Since both the unloaded and loaded powders were obtained using a Buchi Mini Spray Drier with the same operating conditions, the loaded powders containing maltodextrin were observed under a light microscope to determine if the difference in particle size was due to the agglomeration of powder particles

in the dryer chamber. It appeared as though the particles were stuck together which explains the marked difference between the unloaded and loaded sample particle size. It is possible that the maltodextrin formulations had surface oil (low emulsion stability and low volatile retention) which could have contributed to particle stickiness and agglomeration (O'Callaghan and Hogan 2013). For the unloaded powder, there is a decrease in particle size with increasing dextrose equivalence. These results are expected as particle size is directly related to viscosity, as the viscosity of the infeed material decreases there is a decrease in particle size (Bangs and Reineccius 1982).

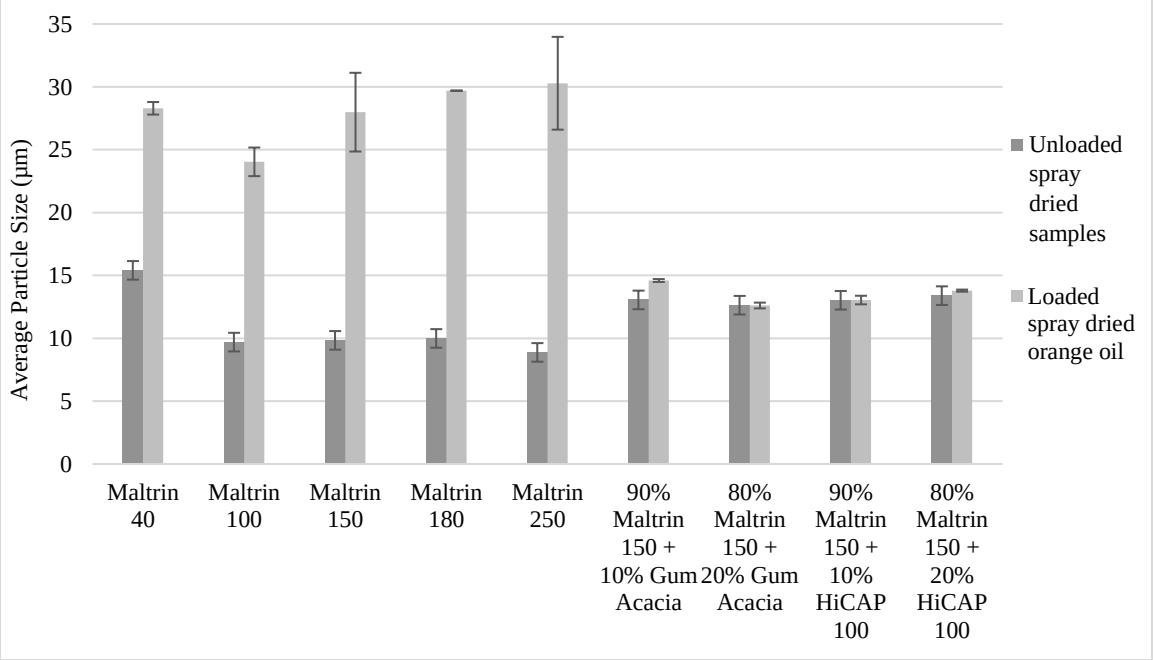



Figure 4.3: The influence of the carrier wall material on the particle size of unloaded (no orange oil) powders and loaded spray dried oil powders

**Absolute Density**

The absolute density of a powder sheds light on the void space available for oxygen, water and volatiles to move in and out of the spray dried particle contributing to diffusion and oxidation. The absolute densities do not significantly differ after being equilibrated at differing water activities (Table 4.2 and Table 4.3, Appendix 5). However, when

comparing the unloaded to the loaded formulas, the loaded powders are less dense than the unloaded powders. These results are not surprising as spray dried carrier materials usually have a density of about 1.6 g/cc while orange oil is less dense weighing only ~0.84 g/cc. At a 20% orange oil load in the loaded formulation we would expect the loaded powders to be slightly less dense (~1.45 g/cc) than the unloaded powders. Overall, the density of the powders produced in this study are denser than previous research on spray dried powders (~1.2 g/cc) (Drusch and others 2009). The variation in density is attributed to the type of atomization used in previous research (centrifugal wheel) (Drusch and others 2009). This type of atomization (centrifugal wheel) exhibits more force and shear thereby results a less dense powder (Drusch and others 2009).

Table 4.2: The effect of carrier type and water activity on the absolute density of the unloaded (no orange oil) spray dried powder stored at ambient temperature (water activity of 0.11, 0.33 and 0.53 aw)

| | 0.11 aw | | 0.33 aw | | 0.53 aw | |
|---|---|---|---|---|---|---|
| Composition | Average Density (g/cm3) | Standard Deviation (g/cm3) | Average Density (g/cm3) | Standard Deviation (g/cm3) | Average Density (g/cm3) | Standard Deviation (g/cm3) |
| Maltrin 40 | - | - | 1.51 | 0.08 | - | - |
| Maltrin 100 | - | - | 1.44 | 0.02 | - | - |
| Maltrin 150 | 1.57 | 0.00 | 1.55 | 0.05 | 1.55 | 0.03 |
| Maltrin 180 | - | - | 1.48 | 0.06 | - | - |
| Maltrin 250 | - | - | 1.54 | 0.02 | - | - |
| 90% Maltrin 150 + 10% Gum Acacia | 1.48 | 0.01 | 1.44 | 0.02 | 1.47 | 0.00 |
| 80% Maltrin 150 + 20% Gum Acacia | - | - | 1.43 | 0.01 | - | - |
| 90% Maltrin 150 + 10% HiCAP 100 | 1.52 | 0.01 | 1.47 | 0.00 | 1.47 | 0.01 |
| 80% Maltrin 150 + 20% HiCAP 100 | - | - | 1.44 | 0.04 | - | - |

Table 4.3: The effect of carrier type and water activity on the absolute density of the loaded spray dried orange oil stored at ambient temperature (water activity of 0.11, 0.33 and 0.53 aw)

| | 0.11 aw | | 0.33 aw | | 0.53 aw | |
|---|---|---|---|---|---|---|
| Composition | Average Density (g/cm3) | Standard Deviation (g/cm3) | Average Density (g/cm3) | Standard Deviation (g/cm3) | Average Density (g/cm3) | Standard Deviation (g/cm3) |
| Maltrin 40 | - | - | 1.45 | 0.00 | - | - |
| Maltrin 100 | - | - | 1.48 | 0.02 | - | - |
| Maltrin 150 | 1.52 | 0.02 | 1.53 | 0.01 | 1.48 | 0.00 |
| Maltrin 180 | - | - | 1.55 | 0.01 | - | - |
| Maltrin 250 | - | - | 1.60 | 0.01 | - | - |
| 90% Maltrin 150 + 10% Gum Acacia | 1.37 | 0.02 | 1.34 | 0.01 | 1.30 | 0.01 |
| 80% Maltrin 150 + 20% Gum Acacia | - | - | 1.34 | 0.00 | - | - |
| 90% Maltrin 150 + 10% HiCAP 100 | 1.29 | 0.00 | 1.26 | 0.00 | 1.23 | 0.01 |
| 80% Maltrin 150 + 20% HiCAP 100 | - | - | 1.31 | 0.00 | - | - |

**Moisture Content**

The moisture for the samples stored at each water activity were measured, averaged and recorded (Table 4.4, Appendix 6). As the water activity increased the moisture increased as expected. Spray dried powders typically contain 1-6% moisture and we attribute the differences between the literature values and experimental values of the unloaded powders due to due to the presence of orange oil (Reineccius 2004). Orange oil does not have an affinity to water while the carrier wall materials will absorb more moisture.

Table 4.4: The effect of carrier type and water activity on the average moisture content of the unloaded (no orange oil) powders and loaded spray dried orange oil stored at stored at ambient temperature (water activity of 0.11, 0.33 and 0.53 aw)

| | Unloaded | | Loaded | |
|---|---|---|---|---|
| aw | Average % moisture | Standard Deviation | Average % moisture | Standard Deviation |
| 0.11 aw | 6.26 | 0.72 | 3.34 | 0.09 |
| 0.33 aw | 9.60 | 0.41 | 5.91 | 0.15 |
| 0.53 aw | 9.80 | 0.19 | 7.09 | 0.07 |

**Glass Transition**

Glass transition has been used to predict the molecular mobility of spray dried materials (Kilburn and others 2005; Kilburn and others 2004). The glass transition temperature of the unloaded and loaded powders decreased with increasing dextrose equivalence of carrier matrices containing Maltrin alone (Table 4.5 and 4.6, Appendix 7). The Tg among the blends of carrier wall material increased with decreasing proportion of Maltrin 150 (lower molecular weight carrier material). Both of these results are expected as the addition of low molecular weight polymers or higher dextrose equivalent maltodextrin to the carrier matrix should decrease the Tg according to the Fox and Flory Equation (Townrow and others 2010). When comparing the Tg of the unloaded powder Tg to the Tg of the loaded powders, they did not significantly differ suggesting that the addition of active material does not affect the Tg of the matrix (Table 4.5 and Table 4.6, Appendix 7).

Tg is a function of water activity and our results confirm that Tg decreases linearly with water activity (Table 4.5 and Table 4.6) (Kilburn and others 2004). We attribute differences in glass transition temperatures from other studies as there is not a standard method of reporting (can report the Tg onset, Tg midpoint or Tg endset). Therefore, the differences between the Tg can range between 10-30°C depending how the Tg is chosen (Roos and Drusch 2015).

Table 4.5: The effect of carrier type and water activity on the glass transition of the unloaded spray dried powder stored at ambient temperature (water activity of 0.11, 0.33 and 0.53 aw)

| | 0.11 aw | | 0.33 aw | | 0.53 aw | |
|---|---|---|---|---|---|---|
| Composition | Average Tg (°C) | Standard Deviation | Average Tg (°C) | Standard Deviation | Average Tg (°C) | Standard Deviation |
| Maltrin 40 | - | - | 77.1 | 3.77 | - | - |
| Maltrin 100 | - | - | 72.7 | 0.84 | - | - |
| Maltrin 150 | 79.2 | 0.88 | 69.8 | 2.64 | 72.4 | 0.70 |
| Maltrin 180 | - | - | 65.1 | 0.74 | - | - |
| Maltrin 250 | - | - | 63.1 | 1.53 | - | - |
| 90% Maltrin 150 + 10% Gum Acacia | 82.1 | 8.38 | 78.6 | 1.34 | 73.6 | 1.27 |
| 80% Maltrin 150 + 20% Gum Acacia | - | - | 80.7 | 1.63 | - | - |
| 90% Maltrin 150 + 10% HiCAP 100 | 86.5 | 2.21 | 82.3 | 0.14 | 74.7 | 0.38 |
| 80% Maltrin 150 + 20% HiCAP 100 | - | - | 82.9 | 0.97 | - | - |

Table 4.6: The effect of carrier type and water activity on the glass transition of the loaded spray dried orange oil stored at 20°C (water activity of 0.11, 0.33 and 0.53 aw)

| | 0.11 aw | | 0.33 aw | | 0.53 aw | |
|---|---|---|---|---|---|---|
| Composition | Average Tg (°C) | Standard Deviation | Average Tg (°C) | Standard Deviation | Average Tg (°C) | Standard Deviation |
| Maltrin 40 | - | - | 78.0 | 1.42 | - | - |
| Maltrin 100 | - | - | 75.9 | 2.58 | - | - |
| Maltrin 150 | 77.6 | 0.70 | 74.0 | 1.02 | 73.3 | 0.76 |
| Maltrin 180 | - | - | 73.8 | 3.03 | - | - |
| Maltrin 250 | - | - | 73.1 | 3.61 | - | - |
| 90% Maltrin 150 + 10% Gum Acacia | 79.0 | 0.49 | 75.3 | 1.96 | 75.0 | 0.04 |
| 80% Maltrin 150 + 20% Gum Acacia | - | - | 75.1 | 0.13 | - | - |
| 90% Maltrin 150 + 10% HiCAP 100 | 79.5 | 0.58 | 75.1 | 1.31 | 75.0 | 0.50 |
| 80% Maltrin 150 + 20% HiCAP 100 | - | - | 75.6 | 0.74 | - | - |

**Size of Molecular Voids**

Generally, as the size of molecular voids increases, the ability for oxygen, water and volatiles to move throughout the encapsulated material thereby contributing to diffusion

and oxidation increases. Our results show that the effect of carbohydrate composition on the molecular void size is fairly straightforward as there is a linear decrease in molecular void size as molecular weight of the carrier material decreased due to enhanced molecular packing (Table 4.7, Appendix 8). Previous studies note the similar trends (Kilburn and others 2004; Townrow and others 2007; Townrow and others 2010; Ubbink 2009). The free volume of the unloaded was slightly lower than the loaded samples due to the presence of orange oil. These results are due to the fact that positrons penetrate inside the material at the depth of a few millimeters. If the positron forms in the orange oil it is going to have a different lifetime than if it were to interact with the carrier wall material. In the loaded samples, the positron decay and resultant free volume measurement is a reflection of the weighted average between the two materials. Since the ratio of orange oil to maltodextrin (measured by volatile retention) the samples containing Maltrin alone and the blends of carrier material are the same, we find that the molecular weight of the carrier wall material affects the size and distribution of the size of molecular voids of spray dried encapsulated orange oil (Figure 4.2 and Table 4.7). The effect of water activity on the molecular void size of the encapsulated material is fairly straightforward (Table 4.7, Appendix 8). Previous studies using PALS have shown that carbohydrate composition and water content directly influences the molecular organization of glassy state amorphous carbohydrate matrices (Kilburn and others 2004; Kilburn and others 2005; Townrow and others 2007; Townrow and others 2010). Similar to previous studies, as the relative humidity increased, the average molecular hole size increased (Kilburn and others 2004; Kilburn and others 2005; Townrow and others 2007; Townrow and others 2010). At high water contents,

carbohydrate molecules plasticize the matrix (Kilburn and others 2004; Townrow and others 2007; Townrow and others 2010; Ubbink 2009).

Table 4.7: The effect of carrier type and water activity on the size of molecular voids of unloaded and loaded spray dried orange oil powders measured by PALS at ambient temperature

| | 0.11 aw | | 0.33 aw | | 0.53 aw | |
|---|---|---|---|---|---|---|
| | Unloaded | Loaded | Unloaded | Loaded | Unloaded | Loaded |
| Composition | Size (nm) | Size (nm) | Size (nm) | Size (nm) | Size (nm) | Size (nm) |
| Maltrin 40 | - | - | 0.226 | 0.234 | - | - |
| Maltrin 100 | - | - | 0.221 | 0.224 | - | - |
| Maltrin 150 | 0.213 | 0.224 | 0.220 | 0.223 | 0.237 | 0.229 |
| Maltrin 180 | - | - | 0.216 | 0.221 | - | - |
| Maltrin 250 | - | - | 0.209 | 0.217 | - | - |
| 90% Maltrin 150 + 10% Gum Acacia | 0.210 | 0.222 | 0.221 | 0.233 | 0.249 | 0.235 |
| 80% Maltrin 150 + 20% Gum Acacia | - | - | 0.220 | 0.242 | - | - |
| 90% Maltrin 150 + 10% HiCAP 100 | 0.211 | 0.222 | 0.216 | 0.231 | 0.250 | 0.235 |
| 80% Maltrin 150 + 20% HiCAP 100 | - | - | 0.215 | 0.237 | - | - |

**Limonene Oxidation**

The data for the oxidation of the loaded spray dried orange oil are illustrated in Figures 4.4 – 4.8. Note that the values for the initial limonene oxidation of the encapsulated orange oil (time 0 in plots) were subtracted from the subsequent measurements to account for the initial oxidation of the sample during equilibration to a constant water activity. The rate of increase in oxidation products (LO) with time is represented by a best fit trend line (in Excel).

Previous research indicates that a water activity of 0.33 is a critical point in the stability of encapsulated materials (Ubbink and others 2007). Similar to previous studies, mean molecular weight of the carrier material is one determining factor for oxidative stability of

encapsulation systems. High dextrose equivalent corn syrup solids provide strong protection against oxidation because it is smaller in molecular size so itis better able to pack and form more of a barrier compared to larger molecules (Figure 4.4, Appendix 9) (Reineccius 2004). Higher dextrose equivalent carrier wall materials also contain more free reducing groups in their molecular structure which may act as an antioxidant and contribute to more oxidative stability (Reineccius 2004). In contrast, it is possible that some carrier material's molecular structure impart a pro-oxidant effect on encapsulated materials (Reineccius 2004). It is important to note that one would expect that higher dextrose equivalent maltodextrin and corn syrup solids would provide less protection as the inherent Tg is lower which leads us to believe that Tg is not the sole determinant of oxidation (Reineccius 2004).

The blend formulations displayed superior protection against oxidation over the course of four weeks (Figure 4.5, Appendix 9). Carrier matrices that contain a combination of high and low molecular weight carrier materials have a history of providing superior protection to oxidation due to increased molecular packing (Townrow and others 2007; Ubbink 2009).

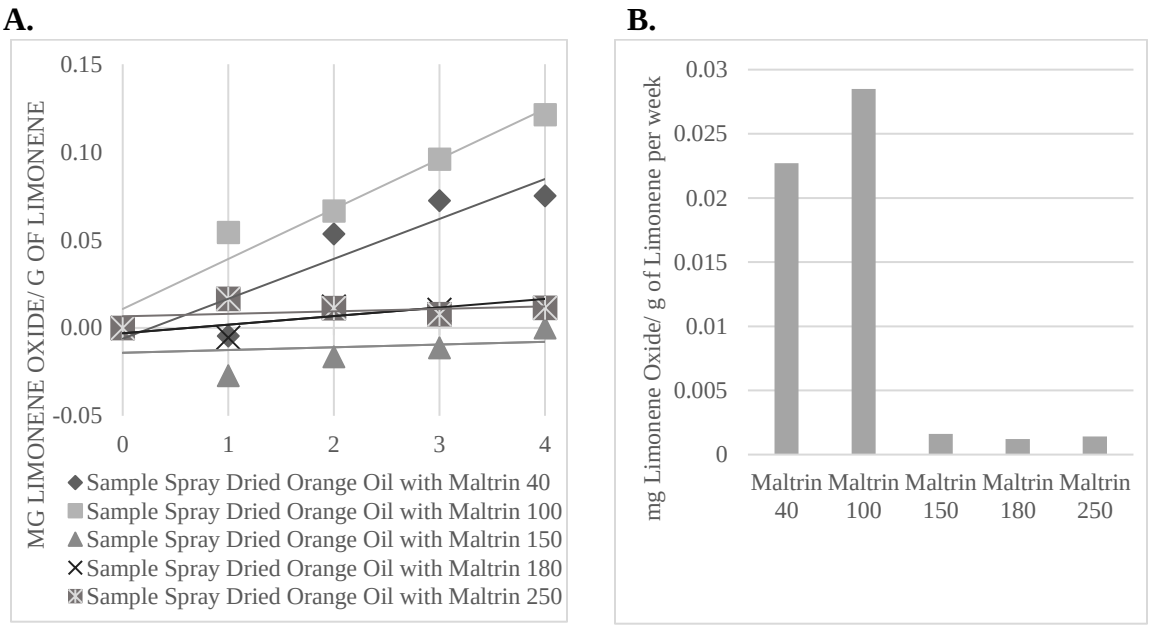



Figure 4.4: **A.** The effect of maltodextrin carrier wall material on the generation of mg of Limonene Oxide per g of Limonene over 4 weeks at ambient temperature and 0.33 aw **B.** The effect of maltodextrin carrier wall material on the rate of orange oil oxidation (generation of mg of Limonene Oxide per g of Limonene per week) at ambient temperature and 0.33 aw

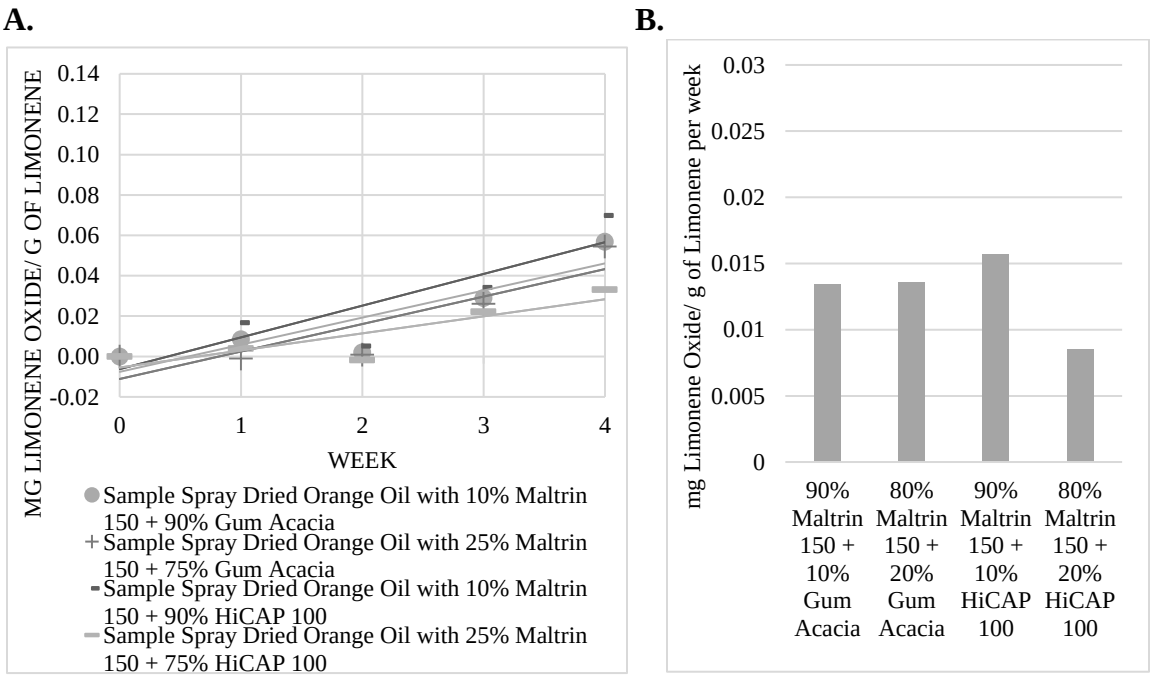
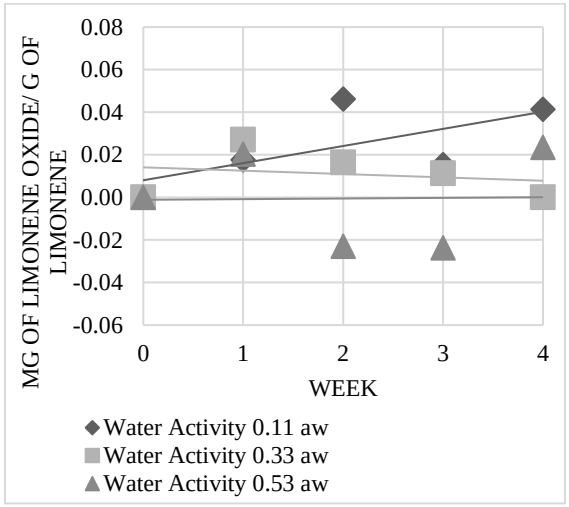



Figure 4.5: **A.** The effect of carrier wall blends on the generation of mg of Limonene Oxide per g of Limonene over 4 weeks of ambient temperature and 0.33 aw **B.** The effect of carrier wall blends on the rate of orange oil oxidation (generation of mg of Limonene Oxide per g of Limonene per week) at ambient temperature and 0.33 aw

Three of the nine unloaded and loaded formulations were stored at three different water activities (0.11, 0.33 and 0.53 aw) (Figures 4.5 – 4.8, Appendix 9). As expected, we see an increase in oxidation as the water activity increases. These results relate to the increase in molecular mobility (measured by Tg) as water activity increases, which leads us to believe that increasing molecular mobility increases orange oil oxidation (Table 4.5 and Table 4.6). Meanwhile, the blends consisting of 90% Maltrin 150 + 10% Gum acacia and 90% Maltrin 150 + 10% HiCAP 100 were relatively stable at 0.11 and 0.53 but have marked differences in oxidation rate at 0.33. These results suggest that that water activity impacts the size of molecular voids of the encapsulation matrix. Although our size of molecular voids increased linearly, Townrow and others (2007) describe the void volume to increase to a certain point and then begin to decrease as the water activity increases. Therefore, it is possible that water activity impacts the diffusion and oxidation of encapsulated active material. Overall, it is evident that the rate of oxidation each encapsulation system differed, highlighting the variability and importance of choosing a carrier wall material that will provide the most stability to the product you are encapsulating.

A.




B.

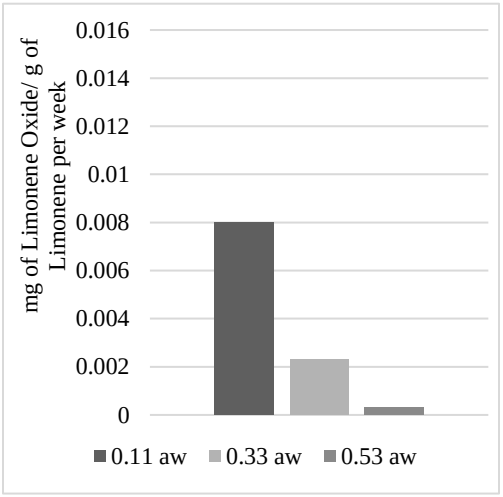
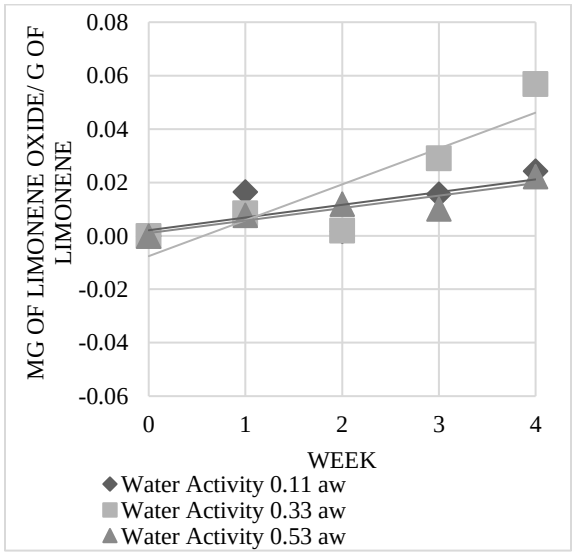



Figure 4.6: **A.** The effect of water activity on the rate of orange oil oxidation (generation of generation of mg of Limonene Oxide per g of Limonene per week) of Maltrin 150 carrier wall material stored at ambient temperature **B.** The influence of water activity on the rate of oxidation of spray dried orange oil with Maltrin 150 as the carrier wall material at ambient temperature

A.




B.

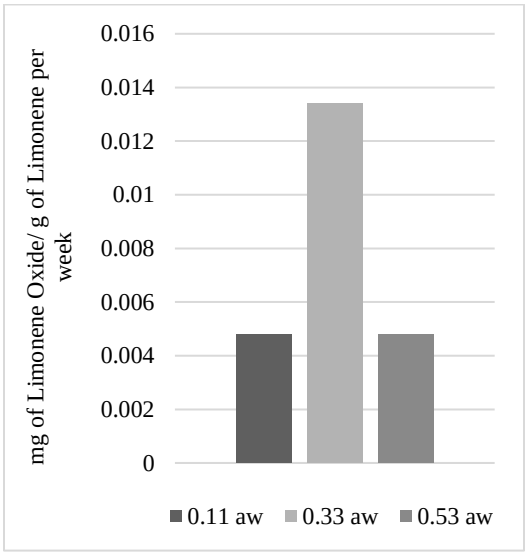



Figure 4.7: **A.** The effect of water activity on the rate of orange oil oxidation (generation of mg of Limonene Oxide per g of Limonene per week) of 90% Maltrin 150 and 10% Gum Acacia carrier wall material stored at ambient temperature **B.** The influence of water activity on the rate of oxidation of spray dried orange oil with 90% Maltrin 150 and 10% Gum Acacia as the carrier material stored at ambient temperature

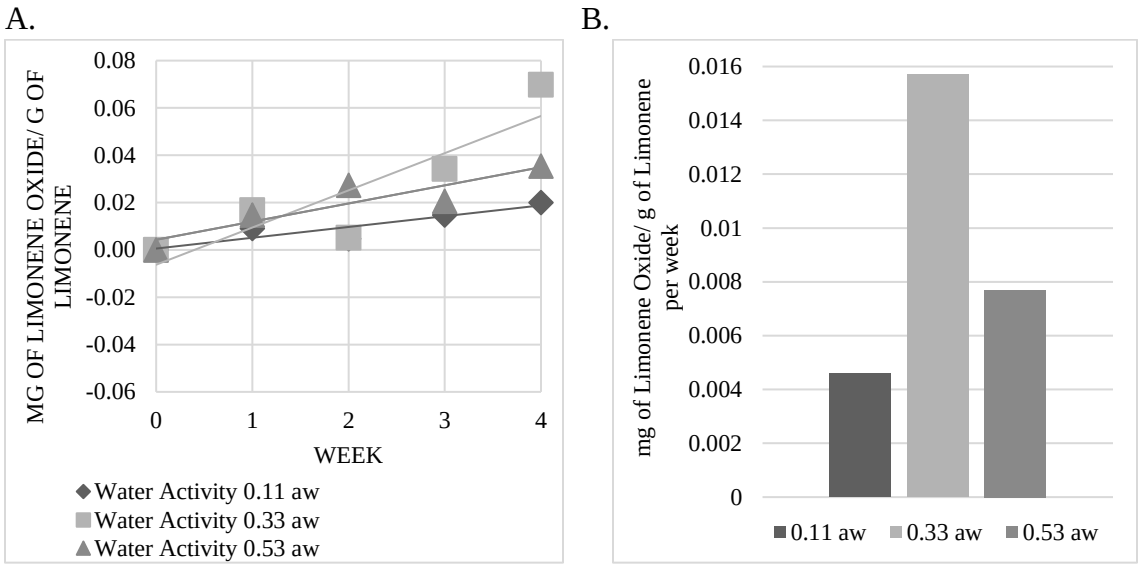



Figure 4.8: **A.** The effect of water activity on the rate of orange oil oxidation (generation of mg of Limonene Oxide per g of Limonene per week) of 90% Maltrin 150 and 10% HiCAP 100 carrier wall material stored at ambient temperature **B.** The influence of water activity on the rate of oxidation of spray dried orange oil with 90% Maltrin 150 and 10% HiCAP 100 as the carrier wall material at ambient temperature

While oxygen diffusivity was not directly measured, it is widely accepted that diffusion is dependent on molecular volume, solubility, and vapor pressure of the permeant, as well as the molecular mobility and free volume of the carrier wall material (Drusch and others 2012; Ubbink 2013; Drusch and others 2009). Thus, an increase in free molecular volume and molecular mobility would allow for oxygen permeation and subsequent oxidation of the active material (Figure 4.4 – 4.8, Table 4.7, Appendix 9) (Reineccius and Yan 2016; Ubbink 2013). The encapsulation systems that exhibit shorter *ortho*-positron lifetimes such (lower molecular weight maltodextrin) are said to be more stable against oxidation and diffusional losses of volatiles due to smaller molecular void size and our results follow the same trend (Figure 4.4 – 4.8, Table 4.7, Appendix 9) (Sahni and others 2016).

The barrier properties of the wall material of encapsulation systems are governed by the matrix composition, water activity and therefore size of molecular voids (Kilburn and

others 2005). These results further confirm previous study results using PALS which show that carbohydrate composition and water content directly influences the molecular organization of amorphous carbohydrate matrices and subsequent oxidative stability (Kilburn and others 2004; Kilburn and others 2005; Townrow and others 2007; Townrow and others 2010).

# Chapter 5: Conclusions

We sought to find a correlation between carrier wall material formulation and molecular mobility to aid in the design of a more stable spray dried encapsulation system. The type of carrier matrix greatly influenced the physical properties and oxidative stability of the spray dried orange oil. The formulations containing maltodextrin as the sole carrier material showed a decrease in viscosity as the molecular weight of the carrier material decreased. Differences between the viscosity of the unloaded and loaded emulsions was due to the addition of orange oil as it is less viscous than water and does not hydrate carrier materials yet contributes to the total percent spray dryer infeed solids. Coalescence occurred in the carrier material formulations that did not contain an emulsifier which led to a large infeed emulsion size. The particle size of the reconstituted powder was consistent among the different types of carrier wall materials due to the shearing action of the atomizer on the spray drier. For the unloaded powder, there is a decrease in particle size with increasing dextrose equivalence. Differences between the unloaded and loaded particle size is due to agglomeration of the loaded powders containing maltodextrin as the sole carrier material. The absolute densities did not significantly differ after being equilibrated at differing water activities however, the loaded powders were less dense than the unloaded powders due to the addition of orange oil which is less dense than carrier material. Spray dried carrier systems that were formulated as a blend containing an emulsifier provided superior reconstituted powder particle size and volatile retention.

With regards to oxidative stability, the smaller molecular weight carbohydrate carrier materials allowed for more dense molecular packing and subsequent a reduction in free molecular volume and oxidation. However, as the molecular weight of the carbohydrate

decreased the Tg also decreased indicating that molecular mobility increased. For the blended formulations, increasing the proportion of Maltrin to emulsifier did not significantly impact the size of molecular voids, molecular mobility or oxidation.

The effect of water activity on the molecular mobility and the size of molecular voids of the encapsulated material was straightforward. As the water content increases, water acts as a plasticizer increasing the molecular mobility and size of molecular voids. The effect of water activity on the oxidation of spray dried carrier systems appeared to increase to a certain point and then decrease with increasing water activity. With these results we conclude that spray dried carrier systems that are formulated as a blend of carbohydrate and emulsifier may provide an ideal balance between molecular mobility and molecular free volume for protection against the oxidation of spray dried orange oil. By understanding the influence of molecular mobility and free volume on the oxidation of orange oil we can more effectively encapsulate flavors to increase the value and shelf life of foods.

# Chapter 6: Future Research

Our analysis is based on the molecular free volume size and the way it changes with molecular weight of the carrier material and water activity. It would be advantageous to examine the void size distribution so that we can better understand the mechanism of molecular void formation as well as the permeability of permeates through the encapsulation matrix.

If this research were to be repeated, we would address one limitation of this study by evaluate the performance of the different wall materials based on viscosity. Viscosity has a direct impact on stability because as viscosity increases the diffusion of volatiles out of the carrier matrix decreases. Evaluating performance based on viscosity would directly relate to the spray dried flavor industry as we would be able to better pin point the balance between throughput and volatile retention.

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# Chapter 7: Appendices

## Appendix 1 (Chapter 4)

**Table 7.1:** Unloaded infeed viscosity

| Composition | Spindle # Used | Speed (rpm) | Reading | Factor | Viscosity (cP) |
|---|---|---|---|---|---|
| Maltrin 40 | H1 | 10 | 9 | 5 | 45 |
| Maltrin 100 | H1 | 10 | 7 | 5 | 35 |
| Maltrin 150 | H1 | 10 | 5 | 5 | 25 |
| Maltrin 180 | H1 | 10 | 4 | 5 | 20 |
| Maltrin 250 | H1 | 10 | 3 | 5 | 15 |
| 90% Maltrin 150 + 10% Gum Acacia | H1 | 10 | 4.5 | 5 | 22.5 |
| 80% Maltrin 150 + 20% Gum Acacia | H1 | 10 | 5 | 5 | 25 |
| 90% Maltrin 150 + 10% HiCAP 100 | H1 | 10 | 4.5 | 5 | 22.5 |
| 80% Maltrin 150 + 20% HiCAP 100 | H1 | 10 | 5 | 5 | 25 |

**Table 7.2:** Loaded infeed orange oil emulsion viscosity

| Composition | Spindle # Used | Speed (rpm) | Reading | Factor | Viscosity (cP) |
|---|---|---|---|---|---|
| Maltrin 40 | H1 | 10 | 7 | 5 | 35 |
| Maltrin 100 | H1 | 10 | 5 | 5 | 25 |
| Maltrin 150 | H1 | 10 | 5 | 5 | 25 |
| Maltrin 180 | H1 | 10 | 4 | 5 | 20 |
| Maltrin 250 | H1 | 10 | 3 | 5 | 15 |
| 90% Maltrin 150 + 10% Gum Acacia | H1 | 10 | 4 | 5 | 20 |
| 80% Maltrin 150 + 20% Gum Acacia | H1 | 10 | 4 | 5 | 20 |
| 90% Maltrin 150 + 10% HiCAP 100 | H1 | 10 | 4 | 5 | 20 |
| 80% Maltrin 150 + 20% HiCAP 100 | H1 | 10 | 4 | 5 | 20 |

## Appendix 2 (Chapter 4)

**Table 7.3:** Infeed orange oil emulsion size

| Composition | Transmittance | Particle Size (µm) | Average Particle Size (µm) | Standard Deviation (µm) | CV (%) |
|---|---|---|---|---|---|
| Maltrin 40 | 85.7% | 32.76 | 32.76 | 0.00 | 0.00 |
| Maltrin 100 | 81.6% | 47.50 | 47.50 | 0.00 | 0.00 |
| Maltrin 150 | 86.4% | 43.35 | 43.35 | 0.00 | 0.00 |
| Maltrin 180 | 83.6% | 51.56 | 51.56 | 0.00 | 0.00 |
| Maltrin 250 | 84.7% | 49.34 | 49.34 | 0.00 | 0.00 |
| 90% Maltrin 150 + 10% Gum Acacia | 89.2% | 1.20 | 1.19 | 0.01 | 0.96 |
| | 86.5% | 1.18 | | | |
| 80% Maltrin 150 + 20% Gum Acacia | 89.8% | 0.43 | 0.47 | 0.05 | 11.03 |
| | 90.8% | 0.51 | | | |
| 90% Maltrin 150 + 10% HiCAP 100 | 86.6% | 1.14 | 1.15 | 0.02 | 1.89 |
| | 86.1% | 1.17 | | | |
| 80% Maltrin 150 + 20% HiCAP 100 | 87.4% | 0.78 | 0.78 | 0.01 | 1.30 |
| | 86.8% | 0.77 | | | |

**Table 7.4:** Reconstituted powder particle size

| Composition | Transmittance | Particle Size (µm) | Mean Particle Size (µm) | Standard Deviation (µm) | CV (%) |
|---|---|---|---|---|---|
| Maltrin 40 | 88.5% | 2.14 | 2.15 | 0.01 | 0.61 |
| | 88.9% | 2.16 | | | |
| Maltrin 100 | 89.7% | 2.22 | 2.17 | 0.08 | 3.46 |
| | 89.2% | 2.12 | | | |
| Maltrin 150 | 89.0% | 2.19 | 2.43 | 0.34 | 13.95 |
| | 90.2% | 2.67 | | | |
| Maltrin 180 | 90.4% | 3.26 | 3.32 | 0.08 | 2.44 |
| | 85.8% | 3.38 | | | |
| Maltrin 250 | 90.1% | 2.10 | 2.21 | 0.16 | 7.27 |
| | 88.5% | 2.32 | | | |
| 90% Maltrin 150 + 10% Gum Acacia | 86.2% | 1.73 | 1.74 | 0.02 | 1.28 |
| | 89.1% | 1.76 | | | |
| 80% Maltrin 150 + 20% Gum Acacia | 90.1% | 1.54 | 1.42 | 0.17 | 12.26 |
| | 89.2% | 1.30 | | | |
| 90% Maltrin 150 + 10% HiCAP 100 | 86.7% | 1.53 | 1.90 | 0.52 | 27.27 |
| | 90.1% | 2.27 | | | |
| 80% Maltrin 150 + 20% HiCAP 100 | 86.6% | 2.28 | 1.72 | 0.79 | 46.05 |
| | 89.2% | 1.16 | | | |

**Appendix 3 (Chapter 4)**

**Table 7.5:** Volatile retention of spray dried orange oil

| Composition | Sample # | Sample weight (g) | T1 Distilled oil (mL) | T1 Distilled oil (g) | T1 Volatile oil retention | Sample weight (g) | T2 Distilled oil (mL) | T2 Distilled oil (g) | T2 Volatile oil retention | Average Volatile oil retention (%) | Standard Deviation | CV (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Maltrin 40 | A1 | 5.07 | 0.4 | 0.34 | 26.88 | 5.01 | 0.4 | 0.34 | 27.22 | 27.05 | 0.24 | 0.89 |
| Maltrin 100 | A2 | 5.05 | 0.4 | 0.34 | 26.99 | 5.01 | 0.4 | 0.34 | 27.21 | 27.10 | 0.15 | 0.56 |
| Maltrin 150 | A3 | 5.02 | 0.4 | 0.34 | 27.17 | 5.07 | 0.4 | 0.34 | 26.90 | 27.04 | 0.19 | 0.71 |
| Maltrin 180 | A4 | 5.04 | 0.4 | 0.34 | 27.04 | 5.09 | 0.4 | 0.34 | 26.79 | 26.91 | 0.17 | 0.65 |
| Maltrin 250 | A5 | 4.05 | 0.3 | 0.26 | 25.23 | 4.02 | 0.3 | 0.26 | 25.45 | 25.34 | 0.16 | 0.64 |
| 90% Maltrin 150 + 10% Gum Acacia | B1 | 5.00 | 1.3 | 1.11 | 88.57 | 5.02 | 1.3 | 1.11 | 88.25 | 88.41 | 0.22 | 0.25 |
| 80% Maltrin 150 + 20% Gum Acacia | B2 | 5.05 | 1.3 | 1.11 | 87.76 | 5.05 | 1.3 | 1.11 | 87.82 | 87.79 | 0.04 | 0.05 |
| 90% Maltrin 150 + 10% HiCAP 100 | C1 | 5.11 | 1.3 | 1.11 | 86.68 | 5.14 | 1.3 | 1.11 | 86.26 | 86.47 | 0.29 | 0.34 |
| 80% Maltrin 150 + 20% HiCAP 100 | C2 | 5.08 | 1.3 | 1.11 | 87.16 | 5.18 | 1.3 | 1.11 | 85.53 | 86.34 | 1.15 | 1.33 |

## Appendix 4 (Chapter 4)

**Table 7.6:** Particle size of the unloaded spray dried powder

| Composition | Transmittance | Mean Particle Size (µm) | Average Mean Particle Size (µm) | Standard Deviation (µm) | CV (%) |
|---|---|---|---|---|---|
| Maltrin 40 | 96.8% | 15.78 | 15.40 | 0.54 | 3.50 |
| | 96.6% | 15.02 | | | |
| Maltrin 100 | 97.4% | 9.71 | 9.70 | 0.02 | 0.21 |
| | 97.7% | 9.68 | | | |
| Maltrin 150 | 97.6% | 9.95 | 9.83 | 0.17 | 1.72 |
| | 97.6% | 9.71 | | | |
| Maltrin 180 | 97.8% | 9.83 | 9.99 | 0.21 | 2.15 |
| | 97.9% | 10.14 | | | |
| Maltrin 250 | 97.8% | 8.94 | 8.88 | 0.09 | 0.98 |
| | 97.1% | 8.81 | | | |
| 90% Maltrin 150 + 10% Gum Acacia | 97.5% | 13.01 | 13.05 | 0.06 | 0.45 |
| | 98.7% | 13.09 | | | |
| 80% Maltrin 150 + 20% Gum Acacia | 98.1% | 12.65 | 12.63 | 0.02 | 0.17 |
| | 97.1% | 12.61 | | | |
| 90% Maltrin 150 + 10% HiCAP 100 | 98.1% | 12.98 | 13.02 | 0.06 | 0.49 |
| | 98.0% | 13.07 | | | |
| 80% Maltrin 150 + 20% HiCAP 100 | 98.2% | 13.33 | 13.39 | 0.08 | 0.61 |
| | 97.5% | 13.45 | | | |

**Table 7.7:** Particle size of spray dried orange oil

| Composition | Transmittance | Mean Particle Size (µm) | Average Mean Particle Size (µm) | Standard Deviation (µm) | CV (%) |
|---|---|---|---|---|---|
| Maltrin 40 | 97.1% | 28.65 | 28.30 | 0.50 | 1.77 |
| | 97.1% | 27.94 | | | |
| Maltrin 100 | 98.2% | 23.23 | 24.04 | 1.14 | 4.73 |
| | 98.2% | 24.84 | | | |
| Maltrin 150 | 97.1% | 24.58 | 27.99 | 3.13 | 11.19 |
| | 97.9% | 28.65 | | | |
| Maltrin 180 | 97.2% | 30.74 | 29.70 | 0.74 | 2.48 |
| | 98.0% | 29.70 | | | |
| Maltrin 250 | 97.7% | 27.68 | 30.29 | 3.69 | 12.19 |
| | 97.8% | 32.90 | | | |
| 90% Maltrin 150 + 10% Gum Acacia | 97.1% | 14.68 | 14.59 | 0.12 | 0.80 |
| | 98.2% | 14.51 | | | |
| 80% Maltrin 150 + 20% Gum Acacia | 98.2% | 12.77 | 12.61 | 0.23 | 1.83 |
| | 97.4% | 12.44 | | | |
| 90% Maltrin 150 + 10% HiCAP 100 | 97.7% | 13.28 | 13.04 | 0.34 | 2.61 |
| | 97.9% | 12.80 | | | |
| 80% Maltrin 150 + 20% HiCAP 100 | 97.7% | 13.73 | 13.79 | 0.08 | 0.61 |
| | 98.2% | 13.45 | | | |

**Appendix 5 (Chapter 4)**

**Table 7.8:** Density of unloaded spray dried powders stored at 0.11 aw

| Composition | Density (g/cm3) | Standard Deviation |
|---|---|---|
| Maltrin 150 | 1.57 | 0.00 |
| 90% Maltrin 150 + 10% Gum Acacia | 1.48 | 0.01 |
| 90% Maltrin 150 + 10% HiCAP 100 | 1.52 | 0.01 |

**Table 7.9:** Density of unloaded spray dried powders stored at 0.33 aw

| Composition | Density (g/cm3) | Standard Deviation |
|---|---|---|
| Maltrin 40 | 1.51 | 0.08 |
| Maltrin 100 | 1.44 | 0.02 |
| Maltrin 150 | 1.55 | 0.05 |
| Maltrin 180 | 1.48 | 0.06 |
| Maltrin 250 | 1.54 | 0.02 |
| 90% Maltrin 150 + 10% Gum Acacia | 1.44 | 0.02 |
| 80% Maltrin 150 + 20% Gum Acacia | 1.43 | 0.01 |
| 90% Maltrin 150 + 10% HiCAP 100 | 1.47 | 0.00 |
| 80% Maltrin 150 + 20% HiCAP 100 | 1.44 | 0.03 |

**Table 7.10:** Density of unloaded spray dried powders stored at 0.53 aw

| Composition | Density (g/cm3) | Standard Deviation |
|---|---|---|
| Maltrin 150 | 1.55 | 0.03 |
| 90% Maltrin 150 + 10% Gum Acacia | 1.47 | 0.00 |
| 90% Maltrin 150 + 10% HiCAP 100 | 1.47 | 0.01 |

**Table 7.11:** Density of loaded spray dried orange oil stored at 0.11 aw

| Composition | Density (g/cm3) | Standard Deviation |
|---|---|---|
| Maltrin 150 | 1.52 | 0.02 |
| 90% Maltrin 150 + 10% Gum Acacia | 1.37 | 0.02 |
| 90% Maltrin 150 + 10% HiCAP 100 | 1.29 | 0.00 |

**Table 7.12:** Density of loaded spray dried orange oil stored at 0.33 aw

| Composition | Density (g/cm3) | Standard Deviation |
|---|---|---|
| Maltrin 40 | 1.45 | 0.00 |
| Maltrin 100 | 1.48 | 0.02 |
| Maltrin 150 | 1.53 | 0.01 |
| Maltrin 180 | 1.55 | 0.01 |
| Maltrin 250 | 1.60 | 0.01 |
| 90% Maltrin 150 + 10% Gum Acacia | 1.34 | 0.01 |
| 80% Maltrin 150 + 20% Gum Acacia | 1.34 | 0.00 |
| 90% Maltrin 150 + 10% HiCAP 100 | 1.26 | 0.00 |
| 80% Maltrin 150 + 20% HiCAP 100 | 1.31 | 0.00 |

**Table 7.13:** Density of loaded spray dried orange oil stored at 0.33 aw

| Composition | Density (g/cm3) | Standard Deviation |
|---|---|---|
| Maltrin 150 | 1.48 | 0.00 |
| 90% Maltrin 150 + 10% Gum Acacia | 1.30 | 0.01 |
| 90% Maltrin 150 + 10% HiCAP 100 | 1.23 | 0.01 |

**Appendix 6 (Chapter 4)**

**Table 7.14:** Moisture content of unloaded spray dried powders stored at 0.11 aw

| Composition | % moisture | Standard Deviation |
|---|---|---|
| Maltrin 150 | 6.11 | 1.13 |
| 90% Maltrin 150 + 10% Gum Acacia | 6.16 | 0.49 |
| 90% Maltrin 150 + 10% HiCAP 100 | 6.51 | 0.54 |

**Table 7.15:** Moisture content of unloaded spray dried powders stored at 0.33 aw

| Composition | % moisture | Standard Deviation |
|---|---|---|
| Maltrin 40 | 10.92 | 0.08 |
| Maltrin 100 | 10.43 | 0.51 |
| Maltrin 150 | 9.80 | 0.28 |
| Maltrin 180 | 9.86 | 0.56 |
| Maltrin 250 | 8.98 | 0.74 |
| 90% Maltrin 150 + 10% Gum Acacia | 10.01 | 0.36 |
| 80% Maltrin 150 + 20% Gum Acacia | 10.46 | 0.03 |
| 90% Maltrin 150 + 10% HiCAP 100 | 9.42 | 0.35 |
| 80% Maltrin 150 + 20% HiCAP 100 | 9.55 | 0.59 |

**Table 7.16:** Moisture content of unloaded spray dried powders stored at 0.53 aw

| Composition | % moisture | Standard Deviation |
|---|---|---|
| Maltrin 150 | 9.57 | 0.33 |
| 90% Maltrin 150 + 10% Gum Acacia | 10.04 | 0.70 |
| 90% Maltrin 150 + 10% HiCAP 100 | 9.80 | 0.43 |

**Table 7.17:** Moisture content of loaded spray dried orange oil stored at 0.11 aw

| Composition | % moisture | Standard Deviation |
|---|---|---|
| Maltrin 150 | 3.08 | 0.07 |
| 90% Maltrin 150 + 10% Gum Acacia | 3.50 | 0.09 |
| 90% Maltrin 150 + 10% HiCAP 100 | 3.43 | 0.12 |

**Table 7.18:** Moisture content of loaded spray dried orange oil stored at 0.33 aw

| Composition | % moisture | Standard Deviation |
|---|---|---|
| Maltrin 40 | 7.98 | 0.29 |
| Maltrin 100 | 6.72 | 0.20 |
| Maltrin 150 | 6.28 | 0.07 |
| Maltrin 180 | 5.71 | 0.04 |
| Maltrin 250 | 5.53 | 0.16 |
| 90% Maltrin 150 + 10% Gum Acacia | 5.49 | 0.18 |
| 80% Maltrin 150 + 20% Gum Acacia | 5.29 | 0.07 |
| 90% Maltrin 150 + 10% HiCAP 100 | 5.38 | 0.13 |
| 80% Maltrin 150 + 20% HiCAP 100 | 4.83 | 0.19 |

**Table 7.19:** Moisture content of loaded spray dried orange oil stored at 0.33 aw

| Composition | % moisture | Standard Deviation |
|---|---|---|
| Maltrin 150 | 7.48 | 0.22 |
| 90% Maltrin 150 + 10% Gum Acacia | 6.90 | 0.14 |
| 90% Maltrin 150 + 10% HiCAP 100 | 6.89 | 0.09 |

**Appendix 7 (Chapter 4)**

**Table 7.20:** Tg of unloaded spray dried powders stored at water activity of 0.11 aw

| | | T1 | | | | T2 | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Composition | Sample # | Sample size (mg) | Tg Onset temp. | Tg Endset Temp. | *Tg* | Sample size (mg) | Tg Onset temp. | Tg Endset Temp. | *Tg* | Average Glass Transition | Standard Deviation | CV (%) |
| Maltrin 150 | A3 | 31.7 | 118.8 | 128.1 | 79.8 | 32.0 | 110.6 | 118.7 | 78.6 | 79.2 | 0.9 | 1.1 |
| 90% Maltrin 150 + 10% Gum Acacia | B1 | 36.3 | 50.1 | 130.0 | 76.2 | 45.1 | 126.4 | 117.2 | 88.0 | 82.1 | 8.4 | 10.2 |
| 90% Maltrin 150 + 10% HiCAP 100 | C1 | 41.4 | 107.0 | 117.2 | 88.0 | 47.3 | 86.3 | 109.8 | 84.9 | 86.5 | 2.2 | 2.6 |

**Table 7.21:** Tg of unloaded spray dried powders stored at water activity of 0.33 aw

| | | T1 | | | | T2 | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Composition | Sample # | Sample size (mg) | Tg Onset temp. | Tg Endset Temp. | *Tg* | Sample size (mg) | Tg Onset temp. | Tg Endset Temp. | *Tg* | Average Glass Transition | Standard Deviation | CV (%) |
| Maltrin 40 | A1 | 36.5 | 66.2 | 132.1 | 74.4 | 36.8 | 86.6 | 107.9 | 79.7 | 77.1 | 3.8 | 4.9 |
| Maltrin 100 | A2 | 37.2 | 62.6 | 95.3 | 73.3 | 39.2 | 69.3 | 76.8 | 72.1 | 72.7 | 0.8 | 1.2 |
| Maltrin 150 | A3 | 34.8 | 58.5 | 80.9 | 66.5 | 34.2 | 93.6 | 108.8 | 67.9 | 67.2 | 1.0 | 1.5 |
| Maltrin 180 | A4 | 35.6 | 90.6 | 121.6 | 65.6 | 36.9 | 88.4 | 128.3 | 64.5 | 65.1 | 0.7 | 1.1 |
| Maltrin 250 | A5 | 34.5 | 87.7 | 131.4 | 64.1 | 35.3 | 87.7 | 122.9 | 62.0 | 63.1 | 1.5 | 2.4 |
| 90% Maltrin 150 + 10% Gum Acacia | B1 | 37.6 | 79.2 | 100.9 | 79.6 | 31.5 | 72.6 | 81.5 | 77.7 | 78.6 | 1.3 | 1.7 |
| 80% Maltrin 150 + 20% Gum Acacia | B2 | 33.0 | 120.0 | 128.4 | 81.9 | 37.6 | 79.2 | 100.9 | 79.6 | 80.7 | 1.6 | 2.0 |
| 90% Maltrin 150 + 10% HiCAP 100 | C1 | 32.7 | 102.9 | 109.7 | 82.4 | 35.8 | 126.9 | 130.4 | 82.2 | 82.3 | 0.1 | 0.2 |
| 80% Maltrin 150 + 20% HiCAP 100 | C2 | 37.5 | 106.8 | 114.0 | 83.6 | 30.7 | 113.1 | 125.4 | 82.2 | 82.9 | 1.0 | 1.2 |

**Table 7.22:** Tg of unloaded spray dried powders stored at water activity of 0.53 aw

| | | T1 | | | | T2 | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Composition | Sample # | Sample size (mg) | Tg Onset temp. | Tg Endset Temp. | *Tg* | Sample size (mg) | Tg Onset temp. | Tg Endset Temp. | *Tg* | Average Glass Transition | Standard Deviation | CV (%) |
| Maltrin 150 | A3 | 34.3 | 51.6 | 103.5 | 71.9 | 35.7 | 39.0 | 129.3 | 72.9 | 72.4 | 0.7 | 1.0 |
| 90% Maltrin 150 + 10% Gum Acacia | B1 | 44.0 | 42.6 | 131.6 | 72.7 | 37.0 | 53.8 | 132.8 | 74.5 | 73.6 | 1.3 | 1.7 |
| 90% Maltrin 150 + 10% HiCAP 100 | C1 | 36.8 | 64.3 | 87.0 | 74.4 | 32.8 | 54.4 | 64.1 | 75.0 | 74.7 | 0.4 | 0.5 |

**Table 7.23:** Tg of loaded spray dried powders stored at water activity of 0.11 aw

| | | T1 | | | | T2 | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Composition | Sample # | Sample size (mg) | Tg Onset temp. | Tg Endset Temp. | *Tg* | Sample size (mg) | Tg Onset temp. | Tg Endset Temp. | *Tg* | Average Glass Transition | Standard Deviation | CV (%) |
| Maltrin 150 | A3 | 39.2 | 53.5 | 116.6 | 77.1 | 47.1 | 105.4 | 122.2 | 78.1 | 77.6 | 0.7 | 0.9 |
| 90% Maltrin 150 + 10% Gum Acacia | B1 | 44.4 | 102.4 | 118.5 | 79.4 | 43.5 | 73.8 | 127.9 | 78.7 | 79.0 | 0.5 | 0.6 |
| 90% Maltrin 150 + 10% HiCAP 100 | C1 | 33.9 | 90.4 | 125.4 | 79.9 | 32.9 | 94.9 | 122.1 | 79.1 | 79.5 | 0.6 | 0.7 |

**Table 7.24:** Tg of loaded spray dried powders stored at water activity of 0.33 aw

| | | T1 | | | | T2 | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Composition | Sample # | Sample size (mg) | Tg Onset temp. | Tg Endset Temp. | *Tg* | Sample size (mg) | Tg Onset temp. | Tg Endset Temp. | *Tg* | Average Glass Transition | Standard Deviation | CV (%) |
| Maltrin 40 | A1 | 37.9 | 91.8 | 128.5 | 81.0 | 41.8 | 108.0 | 129.7 | 79.0 | 80.0 | 1.4 | 1.8 |
| Maltrin 100 | A2 | 36.4 | 111.4 | 123.3 | 77.7 | 38.0 | 77.7 | 131.9 | 74.0 | 75.9 | 2.6 | 3.4 |
| Maltrin 150 | A3 | 36.1 | 74.5 | 125.0 | 73.3 | 43.8 | 61.1 | 117.8 | 74.8 | 74.0 | 1.0 | 1.4 |
| Maltrin 180 | A4 | 34.9 | 86.6 | 121.6 | 76.0 | 39.6 | 87.7 | 118.6 | 71.7 | 73.8 | 3.0 | 4.1 |
| Maltrin 250 | A5 | 49.7 | 81.9 | 118.9 | 70.5 | 44.0 | 41.3 | 130.5 | 75.6 | 73.1 | 3.6 | 4.9 |
| 90% Maltrin 150 + 10% Gum Acacia | B1 | 39.5 | 40.6 | 121.7 | 73.9 | 39.3 | 76.1 | 119.1 | 76.7 | 75.3 | 2.0 | 2.6 |
| 80% Maltrin 150 + 20% Gum Acacia | B2 | 32.6 | 37.1 | 122.9 | 75.2 | 39.7 | 55.7 | 57.1 | 75.0 | 75.1 | 0.1 | 0.2 |
| 90% Maltrin 150 + 10% HiCAP 100 | C1 | 34.0 | 72.3 | 121.2 | 74.2 | 33.7 | 58.0 | 103.7 | 76.1 | 75.1 | 1.3 | 1.7 |
| 80% Maltrin 150 + 20% HiCAP 100 | C2 | 32.6 | 76.7 | 113.8 | 76.1 | 37.7 | 44.1 | 123.5 | 75.1 | 75.6 | 0.7 | 1.0 |

**Table 7.25:** Tg of loaded spray dried powders stored at water activity of 0.53 aw

| | | T1 | | | | T2 | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Composition | Sample # | Sample size (mg) | Tg Onset temp. | Tg Endset Temp. | *Tg* | Sample size (mg) | Tg Onset temp. | Tg Endset Temp. | *Tg* | Average Glass Transition | Standard Deviation | CV (%) |
| Maltrin 150 | A3 | 41.4 | 59.1 | 124.2 | 73.8 | 50.6 | 56.6 | 121.0 | 72.7 | 73.3 | 0.8 | 1.0 |
| 90% Maltrin 150 + 10% Gum Acacia | B1 | 32.3 | 37.9 | 124.0 | 74.9 | 34.9 | 47.5 | 127.6 | 75.0 | 75.0 | 0.0 | 0.0 |
| 90% Maltrin 150 + 10% HiCAP 100 | C1 | 34.6 | 41.3 | 122.3 | 74.7 | 28.7 | 28.6 | 103.5 | 75.4 | 75.0 | 0.5 | 0.7 |

**Appendix 8 (Chapter 4)**

**Table 7.26:** Size of molecular voids of unloaded spray dried powders stored at water activity of 0.11 aw

| Sample | Amplitude | Uncertainty | Time #1 (ns) | Fraction 1 | Time #2 (*ortho*-posirton time in ns) | Void Size (nm) | Uncertainty | Fraction 2 | W | Background | Center |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Maltrin 150 | 843720 | 919.8 | 0.460 | 1.104 | 1.327 | 0.213 | 0.015 | 0.149 | 0.392 | 1.320 | 0.440 |
| 90% Maltrin 150 + 10% Gum Acacia | 808079 | 900.2 | 0.464 | 1.076 | 1.306 | 0.210 | 0.016 | 0.152 | 0.395 | 1.290 | 0.431 |
| 90% Maltrin 150 + 10% HiCAP 100 | 824411 | 909.2 | 0.462 | 1.091 | 1.312 | 0.222 | 0.016 | 0.144 | 0.394 | 1.306 | 0.440 |

**Table 7.27:** Size of molecular voids of unloaded spray dried powders stored at water activity of 0.33 aw

| Sample | Amplitude | Uncertainty | Time #1 (ns) | Fraction 1 | Time #2 (*ortho*-positron time in ns) | Void Size (nm) | Uncertainty | Fraction 2 | W | Background | Center |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Maltrin 40 | 829320 | 912.1 | 0.455 | 1.087 | 1.432 | 0.226 | 0.015 | 0.146 | 0.400 | 1.294 | 0.436 |
| Maltrin 100 | 817535 | 905.6 | 0.456 | 1.127 | 1.391 | 0.221 | 0.015 | 0.148 | 0.394 | 1.277 | 0.411 |
| Maltrin 150 | 827823 | 911.2 | 0.457 | 1.116 | 1.381 | 0.220 | 0.016 | 0.144 | 0.393 | 1.299 | 0.421 |
| Maltrin 180 | 834259 | 914.7 | 0.456 | 1.090 | 1.354 | 0.216 | 0.015 | 0.146 | 0.398 | 1.293 | 0.436 |
| Maltrin 250 | 803059 | 897.4 | 0.458 | 1.109 | 1.301 | 0.209 | 0.016 | 0.148 | 0.391 | 1.293 | 0.417 |
| 90% Maltrin 150 + 10% Gum Acacia | 792383 | 891.6 | 0.461 | 1.178 | 1.395 | 0.221 | 0.016 | 0.145 | 0.388 | 1.278 | 0.391 |
| 80% Maltrin 150 + 20% Gum Acacia | 839581 | 917.7 | 0.457 | 1.140 | 1.388 | 0.220 | 0.015 | 0.146 | 0.389 | 1.301 | 0.404 |
| 90% Maltrin 150 + 10% HiCAP 100 | 817372 | 905.5 | 0.460 | 1.115 | 1.350 | 0.216 | 0.016 | 0.147 | 0.396 | 1.317 | 0.420 |
| 80% Maltrin 150 + 20% HiCAP 100 | 808922 | 900.8 | 0.460 | 1.110 | 1.345 | 0.215 | 0.016 | 0.145 | 0.397 | 1.293 | 0.424 |

**Table 7.28:** Size of molecular voids of unloaded spray dried powders stored at water activity of 0.53 aw

| Sample | Amplitude | Uncertainty | Time #1 (ns) | Fraction 1 | Time #2 (*ortho*-positron time in ns) | Void Size (nm) | Uncertainty | Fraction 2 | W | Background | Center |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Maltrin 150 | 844590 | 920.4 | 0.459 | 1.098 | 1.414 | 0.237 | 0.015 | 0.144 | 0.398 | 1.300 | 0.440 |
| 90% Maltrin 150 + 10% Gum Acacia | 829449 | 912.1 | 0.461 | 1.125 | 1.403 | 0.249 | 0.016 | 0.144 | 0.393 | 1.283 | 0.423 |
| 90% Maltrin 150 + 10% HiCAP 100 | 797447 | 894.4 | 0.460 | 1.136 | 1.399 | 0.250 | 0.016 | 0.141 | 0.393 | 1.266 | 0.422 |

**Table 7.29:** Size of molecular voids of loaded spray dried powders stored at water activity of 0.11 aw

| Sample | Amplitude | Uncertainty | Time #1 (ns) | Fraction 1 | Time #2 (*ortho*-positron time in ns) | Void Size (nm) | Uncertainty | Fraction 2 | W | Background | Center |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Maltrin 150 | 796048 | 893.7 | 0.472 | 1.090 | 1.526 | 0.224 | 0.018 | 0.126 | 0.398 | 1.371 | 0.439 |
| 90% Maltrin 150 + 10% Gum Acacia | 723717 | 852.4 | 0.472 | 1.145 | 1.634 | 0.222 | 0.020 | 0.114 | 0.394 | 1.402 | 0.425 |
| 90% Maltrin 150 + 10% HiCAP 100 | 837307 | 916.7 | 0.472 | 1.094 | 1.647 | 0.222 | 0.019 | 0.109 | 0.401 | 1.502 | 0.450 |

**Table 7.30:** Size of molecular voids of loaded spray dried powders stored at water activity of 0.33 aw

| Sample | Amplitude | Uncertainty | Time #1 (ns) | Fraction 1 | Time #2 (*ortho*-positron time in ns) | Void Size (nm) | Uncertainty | Fraction 2 | W | Background | Center |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Maltrin 40 | 776366 | 882.6 | 0.463 | 1.120 | 1.505 | 0.234 | 0.016 | 0.139 | 0.393 | 1.290 | 0.432 |
| Maltrin 100 | 768115 | 877.9 | 0.465 | 1.138 | 1.420 | 0.224 | 0.017 | 0.138 | 0.395 | 1.297 | 0.411 |
| Maltrin 150 | 798176 | 894.8 | 0.461 | 1.108 | 1.412 | 0.223 | 0.016 | 0.138 | 0.396 | 1.293 | 0.436 |
| Maltrin 180 | 778711 | 883.8 | 0.463 | 1.123 | 1.393 | 0.221 | 0.017 | 0.141 | 0.395 | 1.300 | 0.420 |
| Maltrin 250 | 770213 | 879.0 | 0.467 | 1.142 | 1.364 | 0.217 | 0.017 | 0.135 | 0.392 | 1.285 | 0.408 |
| 90% Maltrin 150 + 10% Gum Acacia | 748139 | 866.5 | 0.467 | 1.143 | 1.490 | 0.233 | 0.019 | 0.122 | 0.395 | 1.396 | 0.413 |
| 80% Maltrin 150 + 20% Gum Acacia | 860096 | 929.0 | 0.466 | 1.129 | 1.573 | 0.242 | 0.018 | 0.110 | 0.397 | 1.376 | 0.439 |
| 90% Maltrin 150 + 10% HiCAP 100 | 857207 | 927.3 | 0.464 | 1.133 | 1.479 | 0.231 | 0.018 | 0.118 | 0.395 | 1.424 | 0.434 |
| 80% Maltrin 150 + 20% HiCAP 100 | 837670 | 916.8 | 0.468 | 1.137 | 1.532 | 0.237 | 0.018 | 0.118 | 0.391 | 1.462 | 0.427 |

**Table 7.31:** Size of molecular voids of loaded spray dried powders stored at water activity of 0.53 aw

| Sample | Amplitude | Uncertainty | Time #1 (ns) | Fraction 1 | Time #2 (*ortho*-positron time in ns) | Void Size (nm) | Uncertainty | Fraction 2 | W | Background | Center |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Maltrin 150 | 816650 | 905.1 | 0.465 | 1.111 | 1.463 | 0.229 | 0.017 | 0.132 | 0.395 | 1.281 | 0.440 |
| 90% Maltrin 150 + 10% Gum Acacia | 819192 | 906.6 | 0.462 | 1.117 | 1.512 | 0.235 | 0.017 | 0.122 | 0.398 | 1.400 | 0.451 |
| 90% Maltrin 150 + 10% HiCAP 100 | 751838 | 868.6 | 0.466 | 1.185 | 1.508 | 0.235 | 0.019 | 0.120 | 0.392 | 1.368 | 0.415 |

**Appendix 9 (Chapter 4)**

**Table 7.32:** Oxidation of spray dried orange oil stored at water activity of 0.11 aw over 4 weeks

| | mg Limonene Oxide/ g Limonene | | | | |
|---|---|---|---|---|---|
| Sample | Initial | Week 1 | Week 2 | Week 3 | Week 4 |
| Maltrin 150 | 1.98E-01 | 1.80E-01 | 1.52E-01 | 1.83E-01 | 1.57E-01 |
| 90% Maltrin 150 + 10% Gum Acacia | 8.17E-02 | 9.82E-02 | 8.35E-02 | 9.73E-02 | 1.06E-01 |
| 90% Maltrin 150 + 10% HiCAP 100 | 8.90E-02 | 9.81E-02 | 9.37E-02 | 1.04E-01 | 1.09E-01 |

**Table 7.33:** Oxidation of spray dried orange oil stored at water activity of 0.33 aw over 4 weeks

| | mg Limonene Oxide/ g Limonene | | | | |
|---|---|---|---|---|---|
| Sample | Initial | Week 1 | Week 2 | Week 3 | Week 4 |
| Maltrin 40 | 1.87E-01 | 1.82E-01 | 2.40E-01 | 2.59E-01 | 2.62E-01 |
| Maltrin 100 | 1.89E-01 | 2.43E-01 | 2.55E-01 | 2.85E-01 | 3.10E-01 |
| Maltrin 150 | 1.98E-01 | 1.71E-01 | 1.82E-01 | 1.87E-01 | 1.98E-01 |
| Maltrin 180 | 2.22E-01 | 2.07E-01 | 2.11E-01 | 2.09E-01 | 1.78E-01 |
| Maltrin 250 | 2.81E-01 | 2.98E-01 | 2.92E-01 | 2.89E-01 | 2.92E-01 |
| 90% Maltrin 150 + 10% Gum Acacia | 8.17E-02 | 9.02E-02 | 8.38E-02 | 1.11E-01 | 1.39E-01 |
| 80% Maltrin 150 + 20% Gum Acacia | 7.13E-02 | 7.03E-02 | 7.22E-02 | 9.73E-02 | 1.26E-01 |
| 90% Maltrin 150 + 10% HiCAP 100 | 8.90E-02 | 1.06E-01 | 9.42E-02 | 1.23E-01 | 1.59E-01 |
| 80% Maltrin 150 + 20% HiCAP 100 | 8.53E-02 | 8.92E-02 | 8.35E-02 | 1.07E-01 | 1.18E-01 |

**Table 7.34:** Oxidation of spray dried orange oil stored at water activity of 0.53 aw over 4 weeks

| | mg Limonene Oxide/ g Limonene | | | | |
|---|---|---|---|---|---|
| Sample | Initial | Week 1 | Week 2 | Week 3 | Week 4 |
| Maltrin 150 | 1.98E-01 | 1.78E-01 | 2.21E-01 | 2.22E-01 | 1.74E-01 |
| 90% Maltrin 150 + 10% Gum Acacia | 8.17E-02 | 8.95E-02 | 9.36E-02 | 9.18E-02 | 1.04E-01 |
| 90% Maltrin 150 + 10% HiCAP 100 | 8.90E-02 | 1.04E-01 | 1.16E-01 | 1.10E-01 | 1.24E-01 |